A PRACTICAL TREATISE OF CHEMICAL ANALYSIS: QUALITATIVE

Heinrich Rose

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A PRACTICAL TREATISE

OF

CHEMICAL ANALYSIS.

A

PRACTICAL TREATISE

OF

CHEMICAL ANALYSIS,

INCLUDING

TABLES FOR CALCULATIONS IN ANALYSIS.

BY H. ROSE.

TRANSLATED FROM THE FRENCH AND FROM THE FOURTH GERMAN EDITION.

With Notes and Additions.

BY

A. NORMANDY.

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EDITOR'S PREFACE.

Although a translation of Heinrich Rose's Practical Treatise of Chemical Analysis, by J. Griffin, already appeared in 1831, the work of that most distinguished chemist may be considered, I will venture to say, as unknown to the English public; first, because that translation is now and has been for several years out of print; and secondly, because, from omissions in that former translation, and from additions made by the author in four successive editions, Rose's Treatise is now at least one half more copious than the manual which was published as its translation.

The present work has been written from the French and from the fourth German editions. I have deemed it advisable to do so, because the French translation contains some valuable notes by Professor E. Peligot. I have further presumed to make several additions myself,

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wherever I have thought that I could render the text more clear or more complete, either by explaining the *rationale* of some of the directions given, when they might have proved ambiguous to the student, or, at other times, by adding to the processes indicated by the author, those which have been discovered more lately by other chemists. It is with extreme diffidence that, having resolved to do so, I now offer these remarks; but I have thought that, in a work like the present, which is intended as a book of reference to the analytical chemist, and as a guide to the student in analytical chemistry, I was not departing from the intentions of the author in trying to render it serviceable to a larger number of persons belonging to the latter class. For the same reason I have throughout the work employed the English chemical nomenclature, instead of that of Berzelius, which is used by H. Rose, but which is scarcely known in this country except by the scientific, and even by them never or very seldom made use of in their various publications.

The stars * which are placed at the beginning of a large number of paragraphs, indicate the passages which are wanting in the translation of 1831, in order that the reader may at once see how very incomplete that former translation is, compared with the present edition. The corresponding volume in the former translation contains only 200 pages, the present consists of 746 pages.

H. Rose's Practical Treatise of Analytical Chemistry forms two volumes : the first devoted to qualitative, the second to quantitative analysis. In order to put the British public as soon as possible in possession of that great chemist's admirable work, I have been fortunate enough to prevail upon Messrs. Tegg to publish this first part, which, under the title of "Qualitative Analysis," forms a complete and distinct treatise. The second and last part, upon which I am now assiduously engaged, will appear shortly afterwards.

In conclusion, although it does not become me to speak of the manner in which I have executed the extremely laborious task of editing such a masterly work, I may perhaps be permitted to claim the merit of having performed it most scrupulously, and with the utmost fidelity. I must, however, beg the reader's indulgence for the idiom, which doubtless will be found at times to have a more forensic turn than should be. I have no apology to offer for this defect, except that the work is a translation, and that the English is not my native language. But I trust that, however inelegant or unusual, the mode of expression will not often be found obscure.

The additions of M. Peligot appear in the text, but are placed between inverted commas, and are signed "E. PELIGOT." Those which I have made are placed either in the text between square brackets [ ], or in note, and signed "ED."

A. NORMANDY.

28, *Church Road, De Beauvoir Square, Kingsland Road.*

26*th August*, 1847.

AUTHOR'S PREFACE.

THE conditions which constitute a good manual of Analytical Chemistry are so numerous, that, in composing the present work, I have found it difficult to fulfil them all. Wherefore, the main object which I have kept in view has principally been to write a book which would serve as a guide to those who, being already possessed of sufficient chemical knowledge, are desirous of entering into analytical research.

The First Volume contains an exposition of the order and processes which should be adopted in qualitative analysis. I have given there the means of distinguishing those substances only which are of more frequent occurrence, partly because they are more interesting than those which are rare, but partly also and more especially because the descriptions of the processes which must be resorted to in such cases would have been a great deal too intricate and obscure, had I supposed, in the compound to be examined, the simultaneous presence of all the substances which might possibly be contained in it. Whoever is sufficiently skilled in the qualitative analysis of those bodies which are more ordinarily met with, will be able to discover without difficulty, rarer constituents, if any be present, their behaviour with re-agents being indicated in all chemical manuals, and particularly in Berzelius's Treatise.

The Second Volume indicates the method to be followed for quantitative analysis. Each simple body, except oxygen, is the subject of a separate chapter. In each of these chapters I have described, first, the quantitative determination of the simple body, and of its combinations with oxygen, and next I have shown the means of separating it and its combinations from all the substances which may have been treated of in the preceding chapters, beginning with the simple bodies which produce bases by their union with oxygen; and then I have spoken of those whose combinations manifest acid properties. This appeared to me the most convenient order, as affording the readiest means of finding out, without much difficulty, the plan to be adopted for any given case of analysis. I have but seldom wandered from this rule, and only then, to avoid repetitions; and by adopting it I have been enabled to treat of the analysis of all the silicious minerals in the chapter on Silicium; of all the simple or compound, natural or artificial combinations of sulphur in the chapter on that element; and of the analysis of nearly all gases in the chapter on Hydrogen. The alphabetical table, which I have placed at the end of this work, will be found to facilitate research still more.

The chemical nomenclature which I have made use of, is that employed by Berzelius in his Treatise.

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QUALITATIVE ANALYSIS.

UNIV. OF
CALIFORNIA

Practical Treatise
OF
CHEMICAL ANALYSIS.

PART I.

BEHAVIOUR OF SIMPLE SUBSTANCES, AND OF THEIR SIMPLE COMBINATIONS WITH RE-AGENTS.

HE who wishes to enter into the chemical study of the nature of bodies, that is to say, to render himself capable of performing qualitative analysis, must first acquire a complete knowledge of the behaviour of re-agents with the substances for which he is seeking. I have given, in the Second Part of this volume, a description of the systematic course of operations which should be adopted for the purpose of discovering the constituent parts of simple and of compound combinations; yet, though we may think we have detected these constituent principles, it is nevertheless necessary to submit the substances we may thus have found out to the action of various other tests, in order to put the accuracy of the results obtained beyond doubt.

This First Part will therefore be devoted to the examination of simple bodies, of most of their simpler combinations, especially with oxygen, and the actions of the most characteristic tests upon them. I have in this respect called particular attention to those tests, the actions of which produce decisive appearances, and which, consequently, distinguish and single out the particular substance sought for from those which it may otherwise resemble.

And as the presence of organic matters often modifies the action of tests upon inorganic bodies, I have, in such cases, indicated what methods should be pursued, in order to arrive at conclusive and certain results.

SECTION I.

BASES.

1. POTASH, KO.

PURE potash, or hydrate of potash, is white and somewhat crystalline in texture. Water readily dissolves it with disengagement of heat; its aqueous solution, even diluted, has a very caustic taste; it dissolves the skin of the tongue, and turns reddened litmus paper of a deep blue. Potash quickly absorbs moisture from the air, and deliquesces; it also combines with the carbonic acid contained in the atmosphere, thus by degrees becoming converted into carbonate, and ultimately into bicarbonate of potash. If in that state it be dissolved in water, it will effervesce when supersaturated with acids, which effervescence is due to a disengagement of carbonic acid gas. Potash, heated in a silver crucible, fuses at a heat below redness. When free from carbonic acid it is soluble in alcohol.

The presence of potash in an aqueous solution is detected by the following tests:—

An excess of a concentrated solution of TARTARIC ACID poured in a concentrated solution of potash produces an immediate crystalline precipitate of bitartrate of potash[1], which is a sparingly soluble salt. When the solution of potash is dilute this precipitate appears only after a certain time, but the longer it takes to manifest itself, the more crystalline is its appearance[1]. An excess of a strong acid, such as, for example, muriatic, nitric, sulphuric, or even a solution of oxalic acid, dissolves the precipitate, which effect is not produced by either tartaric or acetic acid. The precipitate formed by tartaric acid is also readily dissolved by the solution of carbonate of potash, of pure potash, of soda and of ammonia; a small quantity of a strong acid poured in that solution, causes the precipitate to reappear, but by adding a larger quantity of acid, the precipitate is re-dissolved.

---

[1] When a re-agent is added to a solution to be tested, care should generally be taken to stir the mixture, not only to insure the diffusion of the re-agent, but likewise because mechanical force has often a great influence upon chemical affinities. Certain solutions may exist together without showing any signs of combination,

* The precipitate of bitartrate of potash is insoluble in strong alcohol; wherefore, when after having produced the said precipitate by pouring an excess of tartaric acid in a solution of potash, and having abandoned it until no further increase of the precipitate takes place, the clear supernatant liquid is poured off, it becomes turbid by the addition of strong alcohol[2].

---

provided they be left at rest; this is especially the case with tartaric acid, an excess of the solution of which may be poured in a solution of potash, without any precipitation taking place, but the moment the mixture is stirred, crystals of bitartrate of potash instantly fall down.—Ed.

[1] Before employing this re-agent, and likewise the chloride of platinum, and the sulphate of alumina mentioned shortly after, it is necessary to make sure that no ammonia or ammoniacal salts are present. This is ascertained by applying some caustic potash to a portion of the solution under examination, and observing whether any odour of ammonia is emitted. If so, the solution under examination must be heated to redness, by which means the ammoniacal salts are decomposed and the ammonia expelled, after which the fixed residuum is to be dissolved in distilled water, and tested for potash by the re-agents above alluded to. The absence of ammonia and ammoniacal salts should first be proved as we have just said, because the behaviour of tartaric acid, of chloride of platinum, and of sulphate of alumina with the salts of ammonia and those of potash is the same. The crystals, especially those of ammoniacal alum, have the same form as those of potash-alum. When the solution under examination contains potash and ammonia, but is very dilute, the presence of the ammonia does not influence the precipitate, because the bitartrate of ammonia, which would be produced would remain in solution, and consequently would not appear, whilst bitartrate of potash, being much less soluble, would fall down.—Ed.

[2] It is therefore advisable to add some alcohol to the liquid which is about to be tested for potash by tartaric acid; for bitartrate of potash being less soluble in alcohol than in water, the delicacy of the test is thereby much increased.—Ed.

An alcoholic solution of BICHLORIDE OF PLATINUM (*chlorure-platinique*) produces in solution of potash, a pale yellow precipitate, which is a double chloride of platinum and potassium, (*chlorure-platinico-potassique*), sparingly soluble. When the quantity of potash is small, it is better to dissolve it in alcohol, and then to pour into it the spirituous solution of chloride of platinum*, because the double chloride of platinum and potassium just alluded to, is altogether insoluble in alcohol[1]. In dilute solutions of potash this precipitate requires a longer time to manifest itself, and then it often has a crystalline appearance, and a somewhat reddish colour. It is good to add a little muriatic acid to the solution of potash. The precipitate thus obtained is not sensibly dissolved by a free acid[2].

HYDROFLUOSILICIC ACID (*acide silicifluorhydrique*) produces in moderately concentrated solutions of potash, a precipitate of silicofluoride of potassium (*silicifluorure-potassique*) sparingly soluble, which is so gelatinous and translucid as to be almost invisible, especially if the solution of potash be very dilute. This gelatinous precipitate takes a long time to separate, and can in reality be recognised only because it is less transparent than the supernatant liquid, and because it is somewhat iridescent; when dried it forms a white powder.

* It is necessary that the hydrofluosilicic acid should be poured in excess in the solution of potash, and not the potash in the acid, because in such a case the free potash would separate gelatinous silicic acid, which would remain insoluble in an excess of hydrofluosilicic acid.

If the solution of potash be concentrated, the addition of hydrofluosilicic acid thereto produces a white turbid appearance, and soon after the transparent gelatinous precipitate begins to separate. In such a case, however, it is not so iridescent as that which has fallen from a very dilute solution. Muriatic acid does not dissolve this precipitate; but after that addition it is no longer transparent.

---

[1] In dilute solutions the addition of alcohol increases also the sensitiveness of chloride of platinum as a test for potash, because the double chloride produced by this re-agent is insoluble in even weak alcohol.—ED.

[2] The sensitiveness of chloride of platinum is augmented by this addition of a little muriatic acid; but when the test employed is tartaric acid, we must bear in mind that no precipitate would be then produced, because bitartrate of potash is soluble in an excess of a strong acid, as has been said.—ED.

An alcoholic solution of CARBAZOTIC ACID (*acide nitropicrique*) produces even in dilute solutions of potash, a crystalline, pale, yellowish precipitate of carbazotate of potash. In order to obtain this precipitate when the quantity of potash is very minute, it is advisable to dissolve the potash in alcohol; because the salt of potash produced, as just said, is insoluble in this menstruum. This re-agent, proposed by Liebig for the detection of potash, is still more delicate than the chloride of platinum solution; in effect, when a solution of potash is so much diluted that a solution of chloride of platinum causes no precipitate, the alcoholic solution of carbazotic acid produces one in the liquid; if not immediately, at least after a short time.

A concentrated solution of SULPHATE OF ALUMINA (*sulfate aluminique*) poured in a concentrated solution of potash, previously saturated with an acid, for which purpose muriatic acid is preferable, produces a precipitate of alum in crystals, which may generally be recognised as regular octahedra; often with truncated angles. The crystals of alum so obtained do not effloresce in the air.

* A solution of PERCHLORIC ACID (*acide oxychlorique*) produces, according to Serullas, in a solution of potash an abundant precipitate of perchlorate of potash, which is insoluble in alcohol.

Before the BLOW-PIPE, according to Harkort, potash may be detected, because the glass of borax, in which pure oxyde of nickel has been dissolved, assumes a blueish colour[1]. According to Fuchs, there is, however, a much better means than that to detect potash by means of the blow-pipe; it consists in putting a small piece of the substance upon a platinum wire bent into a hook, and to fuse it in such a manner that the point of the interior flame touches the fused bead, by which means the exterior flame assumes a purple or violet colour[1].

---

[1] The glass of borax in which pure oxyde of nickel has been dissolved by fusion, is of an orange yellow or reddish colour, which disappears in cooling. A strong dose of oxyde of nickel gives, however, a glass which, when cold, is of a dark red and transparent colour. It is only necessary to take care not to fuse the glass, for a reduction heat destroys that colour, and the glass appears grey, owing to the presence of metallic nickel in a state of extreme division, and which pervades the mass. The oxyde of nickel must be very pure, for if it contains any cobalt, as is frequently the case, the glass would of course become blue, and consequently useless as a test for potash. Mr. Platner (in the *Journ. für pr. Chemie*, xvi. 164), gives the following

The aqueous solutions of the salts of potash behave with the preceding re-agents exactly in the same manner as with pure potash.

An excess of TARTARIC ACID poured in concentrated solutions of the salts of potash, produces the same precipitate of bitartrate of potash as in solution of pure potash. Yet this precipitate does not immediately appear in the solutions of the salts of potash, which are a little less soluble; as, for instance, that of sulphate of potash.

The alcoholic solution of BICHLORIDE OF PLATINUM produces, in concentrated solutions of potash salts, the same pale yellowish precipitate of potassio-chloride of platinum as in the solution of pure potash[2]. When the salt, which is going to be tested for

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method of detecting the presence of cobalt in oxyde of nickel by means of the blow-pipe. The sample under examination is to be fused in borax almost to saturation, and until the mass be opaque. Several samples thus treated are to be put together and melted at a reduction heat with about 1 grain of pure gold (5 centigrammes). The gold takes up the nickel, and becomes lighter in colour. The gold is then to be disengaged by a blow with a hammer, cleaned, and next it is to be submitted to a reduction heat with borax. The little cobalt which the gold may have taken gives a blue colour; and when the reduction of the nickel begins to take place, the glass on cooling becomes greenish. The gold is again to be disengaged as before, and submitted with salt of phosphorus to the oxydating flame, when the characteristic reaction of nickel will appear. The gold may be separated from the nickel and recovered by fusing it with a little lead and oxydating the latter upon a little bone-ash cupel.—ED.

[1] This test is characteristic only, provided there be no soda present, otherwise it will yield the yellow distinctive colour of the soda flame, even though a large quantity of potash may be present.—ED.

[2] It will be seen hereafter, when ammonia is treated of, that this alkali forms also a double chloride of ammonia and platinum, which resembles very much that formed by bichloride of platinum and potash. Dr. Fresenius indicates, as the best method of applying this test, to mix the aqueous solution of the salt of potash with bichloride of platinum, to evaporate the mixture nearly to dryness in a steam or waterbath, and to add alcohol to the residuum, which will leave the double chloride of potassium and platinum undissolved.—ED.

potash, is soluble in alcohol, it is also better to dissolve it in that menstruum, and then to mix it with the alcoholic solution of chloride of platinum.

Hydrofluosilicic acid has the same action on solutions of salts of potash as on that of pure potash.

When carbazotic acid (*acide nitropicrique*) is the test employed to detect extremely small quantities of a salt of potash, it is advisable, if the salt be soluble in alcohol, to dissolve it therein, and to test the alcoholic solution.

A concentrated solution of sulphate of alumina poured in concentrated solutions of most potash salts, determines after a short time the precipitation of crystals of alum. This effect is produced more particularly in concentrated solutions of sulphate and nitrate of potash, and also of chloride of potassium. The solution of sulphate of alumina poured in that of a neutral phosphate, arseniate or borate of potash, produces a bulky precipitate, which is a combination of alumina with the acid of the potash salt operated upon. If the solutions of these salts be acid, crystals of alum are obtained, but most often they appear only after a very long time; their formation may, however, be accelerated by the addition of sulphuric acid. Carbonate of potash and sulphuret of potassium must be previously converted into chloride of potassium, by means of muriatic acid, in order to obtain crystals of alum by the re-action of the solution of sulphate of alumina.

* Perchloric acid produces, in solutions of potash salts, the same precipitate of perchlorate of potash as in solution of pure potash.

Before the blow-pipe, potash may be detected in potash salts in the same manner as pure potash; glass of borax, in which pure oxyde of nickel has been dissolved is coloured blue by these salts. But it is detected still better, at least in most potash salts, by the violet or purple hue which the exterior flame assumes when the potash salt is fused upon a platinum wire, and directing the point of the interior flame upon the fused bead. Chloride, bromide, and iodide of potassium are the salts which more distinctly than others show that characteristic violet colour in the exterior flame of the blow-pipe. This violet flame is even more sensible with these salts than with pure potash. Carbonate and sulphate of potash do not exhibit this phenomenon so strikingly, and phosphate and borate of potash show it still less.

* When concentrated alcohol, previously diluted with nearly its bulk of water, is poured upon a potash salt reduced to powder, if the vessel in which this has been done be placed over a spirit lamp and then heated to ebullition, upon inflaming it, the colour of the flame becomes manifestly blue or violet. Chloride of potassium shows this phenomenon better than any.

* The neutral salts which potash forms with sulphuric, carbonic, phosphoric, arsenic, and boracic acids may be heated either out of or with the contact of the air, without fear of their being volatilised or decomposed, provided always that this be done in a vessel, the nature of which be not capable of exercising a decomposing influence upon them. Chloride of potassium, if heated to redness in contact with the air, is sublimed in the shape of a white smoke, but does not thereby undergo decomposition. It is, however, necessary, in order to volatilise a somewhat considerable quantity of it, to submit it to an extremely high heat, and to employ shallow vessels. This remark applies also to the bromide and iodide of potassium. In the salt which potash produces with oxalic and other organic acids, as well as with nitric, phosphorous, hypo-phosphorous, and several other acids, the action of red heat destroys the acid.

* Some of the solutions of neutral potash-salts do not change the blue colour of litmus paper, and others change reddened litmus paper into blue. Sulphate and nitrate of potash, chloride, bromide, and iodide of potassium dissolved in water belong to this first class; phosphate, arseniate, borate, and carbonate of potash, fluoride and sulphuret of potassium form part of the second class.

* Most of the potash-salts which are more frequently met with, such as sulphate, and nitrate of potash, and chloride of potassium do not contain any water of crystallisation, owing to which

they do not effloresce in the air; yet the potash-salts which contain water of crystallisation do not effloresce either. Small quantities of these salts may often be recognised from their crystalline form. Chloride of potassium crystallises in cubes, the nitrate in prisms, the sulphate in regular six-sided prisms terminated by six-sided pyramids; the carbonate does not crystallise, or at least not readily, and it deliquesces in the air, the moisture of which it greedily absorbs.

Potash forms with only a few acids salts which are insoluble or sparingly soluble in water, and its presence in such salts is then sometimes difficult of detection. Ordinarily this can be done successfully only after having separated the acid from the alkali. But such combinations are of rare occurrence, and they are formed only by very weak acids, or by acids which in a state of purity are insoluble, or difficultly soluble in water. Frequently, then, it is only the acid combinations which are insoluble or nearly so; the neutral combinations are soluble. The combinations of potash with oxyde of uranium, peroxyde of tin, protoxyde of antimony, with antimonious and antimonic acids, tellurous acid, titanic and silicic acids, are insoluble, or of very difficult solution.

The principal re-agents in use for detecting potash in solution, are chloride of platinum and tartaric acid[1]; carbazotic and perchloric acids are less frequently resorted to because they are not so easily procured. Sulphate of alumina and hydrofluosilicic acid are less to be depended upon, especially the latter, which cannot distinguish potash-salts from soda-salts. Chloride of platinum and sulphate of alumina behaving with ammoniacal salts in the same manner as with salts of potash, it is necessary, before either of these tests is applied, to make sure that neither ammonia nor ammoniacal salts are present in the substance to be operated upon.

When potash or the salts of that base are combined in solutions with much organic substance, solution of tartaric acid and of chloride of platinum indicate the presence of potash even in highly coloured liquids. When the object is to ascertain whether an organic substance either in the solid or a pasty state contains any potash, it is to be treated with water, and then by dilute muriatic or by nitric acid. But when the quantity of organic matter is small, it is better to carbonise it in a hessian crucible, or better still in one of platinum, at a heat which should not be too strong, then to pour water or muriatic acid on the charred mass, and then by means of the above tests the presence of potash may be easily ascertained in the filtered solution thus obtained.

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[1] According to Mr. Harting, chloride of platinum may indicate $\frac{1}{210}$ of potash, and concentrated tartaric acid $\frac{1}{220}$ of the same base in solution of nitrate of potash. Slightly reddened litmus paper may detect $\frac{1}{95000}$ of anhydrous potash.—Ed.

2. SODA, NaO.

PURE hydrate of soda in the solid state resembles pure potash very much, but its aqueous solution may be distinguished from one of potash by the following characters; namely, that neither an excess of a concentrated solution of TARTARIC ACID, nor one of BICHLORIDE OF PLATINUM, nor PERCHLORIC ACID, nor CARBAZOTIC ACID, produce any precipitate in soda-solutions. The three acids just mentioned would, however, produce one, if the soda-solution were very concentrated[1].

Solution of SULPHATE OF ALUMINA does not produce any crystals of alum in soda-solutions previously saturated with an acid, but HYDROFLUOSILICIC ACID produces in a soda-solution, provided it be not too dilute, a gelatinous precipitate of silicofluoride of sodium[2].

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[1] The precipitate formed in concentrated solutions of soda by tartaric acid is a bitartrate of soda which, however, is sufficiently distinct from the bitartrate of potash produced by the same re-agent in solution of potash: 1st, By its greater solubility in water. Bitartrate of soda is soluble in 8 parts of cold and 1·8 of boiling water, whilst bitartrate of potash requires 95 parts of cold and 15 of boiling water for its solution. 2ndly, By the difference of form of its crystals. Bitartrate of soda forms small prismatic crystals, whilst the bitartrate of potash falls in crystalline grains. It is perhaps necessary to remark, that bitartrate of soda is like bitartrate of potash insoluble in alcohol; and that the solubility of bitartrate of potash is much increased by the presence of borax, 2 parts of which, in 5 of bitartrate of potash, render the whole soluble in 6 times their weight of boiling water.—ED.

[2] The soda solution should be strong in order to obtain this gelatinous precipitate. —ED.

Before the BLOW-PIPE, soda can most easily be distinguished from potash, because glass of borax, in which pure oxyde of nickel has been dissolved retains its dark red or brown colour unchanged by the addition of soda; but the colour of the exterior flame affords a much more distinct and quite characteristic sign, because when soda is melted upon a platinum wire bent into a hook at the end, and the point of the interior flame directed upon it, as for potash, the exterior flame assumes an intense yellow colour of the same hue as that of a wax-candle burning in a quiet atmosphere. This phenomenon is developed even when soda is mixed with a great quantity of potash.

When soda-salts in a pulverised state are treated by dilute alcohol in the same manner as has been described for potash-salts (p. 8), an intense yellow colour is imparted to the flame of alcohol. Even very small quantities of soda will produce this effect, and this particular hue is not altered, though considerable quantities of a potash-salt be added.

In soda-salts, which are soluble in water, soda may be distinguished from potash in the same manner as for pure soda. The best criterion by which these salts may be distinguished in the solid state, consists in the intense yellow colour which they communicate to the exterior flame of the blow-pipe. Even when the soda-salt is mixed with a potash-salt, the exterior flame assumes nevertheless the characteristic yellow colour, only if the quantity of the potash-salt be considerable, this yellow colour of the flame is less intense. If chloride of sodium be mixed with enough chloride of potassium to form only a twenty-fifth or a thirtieth part of the whole mass, the reaction of the potash, according to Kobell, disappears, and the yellow flame of the soda alone appears.

* Soda-salts behave like potash-salts when heated to redness, except that chloride of sodium is less volatile than chloride of potassium, and iodide of sodium loses a little iodine by the action of a red heat.

Almost all neutral soda-salts crystallised effloresce in the air when they contain water of crystallisation, which is the case with most of them[1]. This phenomenon is exhibited particularly with sulphate, phosphate, arseniate, and carbonate of soda; borate of soda does not show this sensibly. Nitrate of soda, chloride and fluoride of sodium are not efflorescent, because they contain no water of crystallisation.

* The crystalline form of soda-salts is often resorted to as a means of distinguishing inconsiderable portions of soda from potash-salts. Nitrate of soda crystallises in rhomboids, which are not efflorescent, as we have just said; the crystals of carbonate of soda have a tabular form[2] and are efflorescent, whilst carbonate of potash is deliquescent. Chloride of sodium cannot be distinguished from chloride of potassium by the forms of its crystal; both are cubes[3].

Amongst the solutions of neutral salts of soda, those of sulphate and of nitrate of soda, of chloride, bromide, and iodide of sodium, have no action upon litmus paper; solution of phosphate, of arseniate, of borate, and of carbonate of soda, of fluoride, and of sulphuret of sodium, change reddened litmus paper into blue.

Soda forms soluble salts with nearly all acids; a few only yield salts insoluble, or very sparingly soluble, in water. In these latter salts the presence of soda is quite as difficult to detect as that of potash in salts of the same description. The acids which thus produce insoluble or sparingly soluble salts with soda, are almost the same as those which form the like salts with potash. They have been enumerated page 9.

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[1] If dry caustic soda is left exposed to the air, it deliquesces at first, but after a few days it becomes dry again; an effect which does not take place with potash, except after many months' exposure. This difference is owing to this circumstance, that soda produces with carbonic acid a dry efflorescent salt, whilst the salt which potash forms with that acid is a deliquescent one, which in course of time becomes converted into a dry bicarbonate which is not deliquescent.—Ed.

[2] The usual form of carbonate of soda is a rhombic octahedron, the acute angles of which are truncated.—Ed.

[3] This is only the case with chloride of sodium when the solution is left to evaporate spontaneously in the air, in which case solid cubes are obtained; but when they are procured by boiling the solution so as to concentrate it, the form of the crystal of chloride of sodium is a hollow quadrilateral pyramid. Chloride of potassium crystallises in cubes, and both chlorides are anhydrous.—Ed.

In solutions of soda-salts, the presence of soda may be principally detected; because, after having ascertained that an alkali is present, chloride of platinum and tartaric acid produce no reaction in that solution[1]; but the best test for soda, when the substance can be obtained in the solid state, is the yellow colour which it communicates to the flame of the blow-pipe. If it be presumed or supposed that a solution contains both potash and soda simultaneously, a small portion is first to be tested with chloride of platinum; when the conviction has thus been acquired that potash is either present or absent, another portion of the solution is to be evaporated to dryness, and the residuum is to be tried before the blow-pipe. If chloride of platinum have indicated the presence of potash in the solution, and if the exterior flame of the blow-pipe acting upon the evaporated residuum be violet or purple coloured, the solution contains potash only; but if, on the contrary, the exterior flame of the blow-pipe be coloured yellow by this residuum, we may conclude that both potash and soda exist in the solution.

* In performing these experiments, we must not forget that sometimes the wire of platinum alone may communicate a yellowish hue to the flame of the blow-pipe, which may, however, be easily distinguished from that produced by soda-salts. This feeble colouring which the platinum wire imparts to the flame takes place when it has been damped by the perspiration from the hands of the operator or his saliva, previous to making use of it. It would appear that in such cases the chloride of sodium contained in these liquids is the cause of that phenomenon. Should the case offer itself when the operator should be undecided as to whether the yellow tint in question is due to the presence of a soda-salt or to another cause, heating a soda-salt, and preferably to any other the chloride of that base, upon a

platinum wire by the flame of the blow-pipe, would by contrast show the difference which exists between the yellow colour produced by the salt and that which might come from the platinum wire alone, or from other causes.

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[1] This is a negative proof; but should a precipitate be formed by the addition of chloride of potassium or of tartaric acid, it must not be forgotten that ammonia and ammoniacal salts yield a precipitate similar to that produced in potash solutions, and consequently the absence of ammonia and its salts should first be proved.—Ed.

In order to detect soda or soda-salts in solutions which contain much organic matter, the following course should be adopted. The solution is to be evaporated to dryness and then carbonised, when the residuum is abundant, in a hessian crucible, or else in a platinum crucible, which is otherwise preferable; but whatever crucible is made use of, the heat should not be too strong. The carbonised mass is then to be treated by water or muriatic acid, and the whole being thrown on a filter, the presence of soda may be detected by the re-agents, and in the manner above spoken of, either in the filtered liquid or if evaporated to dryness in the residuum left after its evaporation. When an organic matter, either solid or in a pasty state, is supposed to contain much soda, it is also to be burnt, and the carbonised mass is to be treated in the same manner[1].

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[1] Besides the re-agents above mentioned, there is another compound which has lately been recommended for testing soda. It is *antimoniate of potash*. Except this re-agent, there is no other substance known capable of producing a precipitate in moderately dilute solutions of that base. By pouring a solution of the above salt in the liquid tested for soda, a crystalline precipitate is thrown down if that base be present. This precipitate takes place immediately in concentrated solutions, but in dilute ones it does not appear except after some time, and by stirring the mixture briskly, the formation of the precipitate is promoted. In order, however, to obtain the characteristic crystalline precipitate of antimoniate of soda, it is altogether necessary that there should be no other bases present in the solution to be tested. This test can therefore be resorted to only to distinguish soda from potash, or their respective salts from one another. The formation of this precipitate is not interfered with, according to Dr. Fresenius, by neutral salts of potash, except the carbonate of that base, which either prevents or retards it according to the proportion in which it exists in the compound. When therefore the solution to be tested for contains carbonate of potash, it should first be treated by muriatic or acetic acid, so that it should be only feebly alkaline before testing with antimoniate of potash. If the solution be acid, it should first be brought to the neutral state by addition of potash, otherwise the re-agent being decomposed would be precipitated in the shape of hydrated antimonic acid, or of biantimoniate of potash [$KOSb_4O_{10}$]. Salts of ammonia are also precipitated by antimoniate of potash.—Ed.

3. LITHIA, LiO.

[HYDRATE OF LITHIA.]

Pure lithia is a white and crystalline substance, difficultly soluble in water, and it does not deliquesce by exposure[1]. It fuses at a low red heat.

Solutions of the salts of lithia, which are soluble in water, behave with re-agents in the following manner:—

A concentrated solution of CARBONATE OF SODA does not produce an immediate precipitate, even when the solution of the salt of lithia is very strong, but after a long time, a small and granular precipitate of carbonate of lithia is gradually formed. This precipitate is of difficult solution.

A solution of PHOSPHATE OF SODA (*phosphate sodique*) does not produce any precipitate, even after a long time, in solutions of salts of lithia. Yet, if ammonia be then added, an abundant precipitate is produced shortly after. If the whole be made to boil before adding the ammonia, a precipitate is produced which is a double phosphate of soda and lithia (*phosphate sodico-lithique*). When the solution of a salt of lithia, to which solution of phosphate of soda has been added, is evaporated, the liquid becomes turbid whilst the evaporation is going on; but if the mixture be evaporated to dryness, and the residuum treated with water, there remains an insoluble, or sparingly soluble double salt of phosphate of soda and lithia.

A solution of PHOSPHATE OF POTASH (*phosphate potassique*) does not produce any precipitate either, even after a very long time, in solutions of salts of lithia, and though the mixture be made to boil. If the liquor be evaporated to dryness, the dry residuum is completely redissolved by the addition of water. Yet, if after having poured a solution of phosphate of potash in that of a salt of lithia, ammonia be then added, an abundant precipitate is produced shortly after.

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[1] Hydrate of lithia, by exposure, becomes converted into carbonate of lithia, which is much more insoluble still, and in that state it is opaque.—Ed.

An excess of a solution of TARTARIC ACID poured in even very strong solutions of salts of lithia, does not produce any precipitate.

A solution of OXALIC ACID produces no precipitate either.

HYDROFLUOSILICIC ACID yields, with solutions of salts of lithia, a white precipitate of silicofluoride of lithium[1].

Solution of BICHLORIDE OF PLATINUM renders the alcoholic solutions of salts of lithia somewhat turbid, but this turbidness is so slight that it can hardly be seen. If the solution be at all dilute, not the least turbidness can be distinguished.

Solution of SULPHATE OF ALUMINA mixed with concentrated solutions of salts of lithia does not deposit any crystals, even though the precautions which it is necessary to take in such cases, and which are the same as for operating upon salts of potash (page 7) are observed.

* Solution of CARBAZOTIC ACID produces in solutions of salts of lithia a precipitate of carbazotate of lithia (*nitro-picrate lithique*) sparingly soluble.

* Solution of PERCHLORIC ACID has no effect upon solutions of salts of lithia, except the solution of the salt be very strong, and then by the addition of water the precipitate disappears.

Before the BLOW-PIPE lithia can very easily be detected in its salts. When fused upon the bent end of a platinum wire, if the point of the interior flame be directed upon a fused bead, the exterior flame assumes a fine very deep carmine red tinge[2]. Chloride of lithium is of all the salts of lithium that which manifests this phenomenon in the most striking manner[3].

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[1] This silico-fluoride of lithium, according to Berzelius, is difficultly soluble in water, but becomes more so by the addition of an acid, and evaporation causes it to crystallise in small grains, which, viewed through the microscope, are six-sided prisms. When held for a long time in the mouth it has a sourish taste. It fuses at a red heat, but obstinately retains the fluoride of silicium.—ED.

[2] Turner has shown that this reaction can be produced with silicates of lithia, by fusing this salt with a mixture of 1 part of fluor spar in fine powder, and 1½ of sulphate of ammonia or of bisulphate of potash. When the ammoniacal salt is used, the flame is at first greenish, and then red.—ED.

[3] Chloride of strontium gives also a carmine red colour, and so do the salts of lime. Chloride of strontium can however be distinguished, because when, by being

If the salt of lithia be mixed with a potash-salt, the red tinge only is observable, and this, of course, prevents the use of the blow-pipe as a means of detecting potash, even when the quantity of this base exceeds that of lithia. If, on the contrary, the salt of lithia under examination be mixed with a soda-salt, the reaction of the soda alone is manifested, even though the quantity of the lithia predominates; that is to say, the exterior flame is yellow only. The same thing occurs also when the salt of lithia contains at the same time potash and soda-salts.

* Heated to redness, the behaviour of the salts of lithia is the same as with those of potash and soda. Chloride of lithium is a little more volatile than chloride of sodium, but less so than chloride of potassium. It is also to be remarked, that when heated to redness and kept for a long time at that temperature in contact with the air, a small portion of it is decomposed, and produces a little carbonate of lithia[1].

Salts of lithia fuse at a lower temperature than the corresponding potash and soda-salts.

* Many of the salts of lithia are deliquescent, some of them extremely so, a property which may serve to distinguish them from potash and soda-salts. The most deliquescent of all is chloride of lithium[2]. Nitrate of lithia deliquesces also by exposure, but sulphate of lithia is not deliquescent.

Solutions of salts of lithia behave with litmus paper as the corresponding salts of potash and soda.

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heated at the point of the interior flame whilst held there in a forceps with platinum points, the exterior flame becomes, it is true, tinged with a deep carmine red colour; but this takes place only at the beginning, for after the salt has fused not a vestige of the red colour can be seen any longer, whilst with chloride of lithium the red colour remains permanently visible. The carmine red colour given by chloride of lime is less decided, and once fused all colouring of the flame disappears.—Ed.

[1] Most neutral and soluble salts of lithia are not decomposed by being heated to redness out of the contact of the air. Nitrate of lithia, however, which is a neutral deliquescent salt, is decomposed by heat. Platinum is attacked by lithia and its carbonates; therefore when it requires to be melted, a silver crucible should be used. —Ed.

[2] Chloride of lithium is soluble in alcohol, a property which may serve to separate it from chloride of potassium and sodium.—Ed.

Alcoholic solutions of salts of lithia burn with a flame of a fine carmine red colour. The salts of lithia, which are insoluble in alcohol, give this colour to the flame of alcohol only when it is poured on their powder, and the whole stirred with a glass rod, or else when the alcohol is nearly all burnt out.

Lithia forms insoluble or sparingly soluble salts with the same acids which, by uniting with potash or soda, form salts of a similar nature, and its presence in these combinations may be detected in the same manner as that of potash in the corresponding potash-salts (page 9). Lithia gives, however, with certain acids, salts which are insoluble or sparingly soluble, and which with potash and soda form very soluble salts, such as, for instance, carbonic acid, and above all phosphoric acid, when soda is present at the same time. Lithia is of difficult detection in the double phosphate of soda and lithia. This salt fuses before the blow-pipe, but more easily when, after having previously been mixed with soda, it is heated on the bent end of a platinum wire, or on platinum foil. The fused mass is clear, but on cooling it becomes cloudy and crystalline. When this double salt is heated upon charcoal, it is absorbed. The earthy phosphates, as, for example, phosphate of lime and of magnesia, which might be mistaken for the double salt in question, do not fuse with soda upon the wire or the foil of platinum. If a very great excess of soda has been employed, the whole fuses, it is true, but the earthy phosphate may be perfectly distinguished in the fused mass in an undissolved state. If the mixture be fused with soda upon charcoal, the earthy salts are left upon the charcoal, whilst the soda is absorbed[1].

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[1] M. Stein (*Journal für pr. Chemie*) says that—"A very small quantity of chloride of lithium can easily be detected in chloride of sodium, by fusing the mixture of the two chlorides upon the bent end of a platinum wire in the flame of the blow-pipe, plunging the melted mass in tallow, and subsequently lighting it. If there is not too small a proportion of lithium, the red sparkling which characterises lithium may be perceived on the edge of the flame, but the colour becomes more observable precisely when the flame is about being extinguished. This sparkling is very distinct and fine with 1 per cent. of lithium, and may still be seen with $\frac{1}{10}$ per cent."
—Ed.

Lithia is principally to be detected in solutions of salts of lithia, because if it is ascertained that an alkali exists in the liquid operated upon, the addition of carbonate of potash, or of soda, does not form a precipitate in solutions of salts of lithia, unless they be very strong [in which case, after long standing, a white precipitate appears. Ed.] Also, because solutions of tartaric acid and of chloride of platinum do not produce any precipitate or turbidness, which character distinguishes lithia from potash; and lastly, because, if the liquid be mixed with a solution of ammonio-phosphate of soda, an abundant precipitate is formed, after standing a short time, which character distinguishes lithia especially from soda, but from potash also. Its behaviour before the blow-pipe is likewise sufficient to distinguish lithia from the other alkalis.

4. AMMONIA, NH_3.

Pure ammonia dissolved in water has a peculiar penetrating odour, too characteristic to be mistaken. If the quantity of free ammonia contained in water is so feeble that its presence cannot be detected by the smell, it can readily be shown to exist by holding, at the surface of the liquid, a piece of moist reddened litmus paper, or a glass rod, wetted with pretty strong but not fuming muriatic acid; in the first case, the blue colour of litmus paper is restored; in the second, a white cloud is formed above the liquid, even if the quantity of the ammonia is exceedingly minute. If this quantity be more considerable, so that the smell may in some measure indicate its presence, the cloud is thicker, and consequently more visible. The glass rod may be moistened with nitric or with acetic acid, but muriatic acid is a more delicate test.

Aqueous solutions of ammonia, or liquid ammonia, as this solution is called, has a very caustic taste. When concentrated, it dissolves the skin of the tongue, and acts powerfully on reddened litmus paper, which becomes of a deep blue. When kept in glass bottles which are not perfectly stopped, a small quantity becomes in course of time converted into carbonate of ammonia.

A solution of CHLORIDE OF PLATINUM behaves with solution of ammonia exactly as with solution of potash (page 4). The precipitate which is thus produced, and which is an ammonio-chloride of platinum, very much resembles that which the same re-agent produces in solutions of potash and of potash-salts (see the note at page 4).

Concentrated solution of TARTARIC ACID produces in concentrated solutions of ammonia a crystalline precipitate which is a bitartrate of ammonia. If, on the contrary, the solution of ammonia be a dilute one, no precipitate appears. This precipitate is much more soluble in water than bitartrate of potash[1].

A solution of SULPHATE OF ALUMINA behaves with solution of ammonia in the same manner as with solution of potash; and the crystals of alum produced have absolutely the same form as those of potash-alum (see the note, page 3).

Solution of CARBAZOTIC ACID (*acide nitropicrique*) produces no precipitate in ammoniacal solutions, provided they be not very concentrated[2].

HYDROFLUOSILICIC ACID poured in solution of ammonia produces an abundant precipitate of silicic acid, provided a small quantity only of the acid be poured in, so as to leave some ammonia in excess, for otherwise no precipitate is formed.

* Solution of PERCHLORIC ACID (*acide oxychlorique*) produces a precipitate only, if the solution of ammonia is very strong.

The presence of ammonia in the ammoniacal salts which are soluble in water, most of which are inodorous, and amongst which a few only emit a smell resembling that of free ammonia, may be recognised by means of solution of *chloride of platinum* and of ***sulphate of alumina***, just as for the purpose of detecting the corresponding salts of potash, (page 5). An excess of *tartaric acid* poured in concentrated solutions of ammoniacal salts, sometimes produces a precipitate much less considerable than the one formed by the same re-agent in the corresponding potash-salts, but sometimes also no precipitate whatever appears. *Carbazotic* acid behaves in the same manner. *Hydrofluosilicic* and *perchloric acids* produce no precipitate in solutions of ammoniacal salts, unless these solutions be very concentrated.

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[1] Bitartrate of potash requires 95 parts of water at 60° Fahr., and 15 parts at 212° Fahr. for its solution. Before employing chloride of platinum and tartaric acid as re-agents for ammonia, it is of course necessary to make sure that the liquid submitted to analysis does not contain potash, the reaction of these tests with ammonia and potash being very much alike, as we have said before (page 6). This remark applies also to the employment of sulphate of alumina.—ED.

[2] In very concentrated solutions, long flattened brilliant yellow crystals of carbazotate of ammonia fall down, which are very soluble in water.—ED.

* When ammoniacal salts are treated with dilute alcohol in following the directions which have been given for potash-salts, (page 8), they communicate a blue or violet colour to the flame of the alcohol, similar to that which salts of potash produce under the same circumstances; yet the flame becomes of a pure yellow colour by the addition of a minute quantity of a soda-salt.

Almost all ammoniacal salts may be completely volatilized by heat. The sulphate, nitrate, arseniate, and carbonate of ammonia, also the ammoniacal chloride, bromide, iodide, fluoride, and hydrosulphuret, are volatilizable without residuum. Carbonate and muriate of ammonia are, however, the only salts of that series which are volatilizable in contact with air without undergoing decomposition. The phosphate and the borate of ammonia leave a residuum of phosphoric and of boracic acids when heated in glass vessels. Hydrofluate of ammonia (*fluorure ammonique*), when heated in glass vessels, has a powerful action upon them, and is completely volatilizable in platinum vessels only.

When dry ammoniacal salts are triturated in conjunction with alkalies or alkaline earths, the peculiar and well-known odour of ammonia is evolved[1]; carbonates of alkalies and of alkaline earths produce the same effect, except that the odour of ammonia is weaker. Alkalies and alkaline earths, either pure or in the state of carbonates, disengage also the smell of ammonia from the ammoniacal solutions with which they may be mixed. If the quantity of ammonia contained in these solutions be too minute to be perceptible by the smell, a glass rod moistened with muriatic acid, pretty strong but not fuming, is to be held at the surface of the liquid thus mixed with the alkali, or the alkaline earth, when white fumes will immediately be observable; exceedingly slight traces of ammonia may thus be rendered apparent.

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[1] The addition of a little water whilst triturating, favours the disengagement of ammonia.—Ed.

* Extremely minute quantities of ammonia may be detected in a solid combination by triturating it rapidly with hydrate of potash previously pulverised, heating the mixture in a glass tube closed at one end, or in a small beaker glass, and holding a piece of slightly reddened litmus paper (moist), which will recover its blue colour if any ammonia be present[1]. This experiment may be modified by drawing the tube to a point, and plunging it in a vessel containing a dilute solution of subnitrate of mercury (*nitrate mercureux*); the least quantity of ammonia, if present, will turn it black. It is, however, necessary to prevent any potash from passing over in the solution of the subnitrate of mercury, because it would also turn it black; wherefore, if the ammonia can be disengaged from the substance under examination, by applying only the red heat, it is better not to use the potash at all.

Ammonia, like the other alkalies, forms with certain acids, salts which are insoluble, or sparingly soluble in water. It is, however, sufficient to submit those combinations to a red heat to detect the presence of ammonia, for that heat drives it off. In order to detect clearly the presence of ammonia in such compounds, a small portion of the substance is to be placed at the bottom of a tube closed at one end, and if, whilst it is submitted there to a red heat, a glass rod moistened with muriatic acid be held at the orifice, the characteristic white fumes will appear, or if a piece of moist reddened litmus paper be employed instead, it will be turned blue[1].

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[1] Instead of moist reddened litmus paper, a glass rod wetted with muriatic acid, held over the glass containing the heated mixture, will give white fumes if any ammonia be present.—Ed.

The most characteristic tests for ammonia in ammoniacal salts is the smell of ammonia, which caustic potash (or soda) disengages, [more especially if heat be applied. Ed.]; this reaction distinguishes it readily from the other alkalies; bichloride of platinum and sulphate of alumina giving with potash precipitates, which most closely resemble those produced in ammoniacal solutions, may be mistaken for that base[2].

When free ammonia is found mixed with much organic matter in solutions or in pasty masses, the odour emitted at once bespeaks its presence; when, however, ammoniacal salts exist in the mixture, the solution or pasty mass is to be treated by a concentrated solution of potash, and the whole being heated, the ammoniacal smell is disengaged. The process is the same when ammoniacal salts are mixed with dry organic substances. If the solution under examination be too dilute, it must be concentrated by evaporation before treating it with potash[3].

5. BARYTA, BaO.

Pure baryta has a greyish-white colour, and is very easy to pulverise. When water[4] is poured on it, it absorbs it, heat is evolved, and it crumbles down into a white powder (hydrate of baryta). More water converts it into a white crystalline mass, which, when the baryta is pure, is completely soluble in hot water[5]. A concentrated solution of that substance in boiling water, deposits on cooling, crystals of hydrate of baryta, provided the access of air be excluded[6]. Solution of baryta has a caustic, alkaline taste, and a strong blue reaction upon reddened litmus paper. Exposed to the air, it soon attracts carbonic acid, and its surface becomes covered with a pellicle of carbonate of baryta, which is insoluble in water, and gradually falls to the bottom; but as soon as this pellicle falls down, another forms, and so on continually until the whole of the baryta be precipitated as carbonate of that base.

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[1] By moderately heating the paper, the ammonia is volatilised, and the paper reassumes its red colour.—Ed.

[2] Therefore it is well to make sure that potash is not present before testing with these re-agents (see note 1, page 20).—Ed.

[3] All neutral ammoniacal salts hold water in combination; those which are anhydrous always contain an excess of base.—Ed.

[4] The water thus added, must of course be in small quantities, as in slaking lime.—Ed.

[5] Hydrate of baryta is soluble in 20 parts of cold and 3 of boiling water, according to Davy. The vessels in which the solution is operated must be well closed.—Ed.

[6] These crystals are flattened hexagonal prisms, and contain so much water of crystallization as to be double the weight of anhydrous baryta.—Ed.

Hydrate of baryta is soluble in a great quantity of alcohol[1]. Pure baryta does not fuse at a red heat, but hydrate of baryta does[2].

However diluted the solutions of baryta-salts may be, when dilute sulphuric acid or the solution of a sulphate is poured into them, a white precipitate of sulphate of baryta is produced, which the addition of free acid does not dissolve; for this purpose muriatic or nitric acid are preferable. * If the solution of a baryta-salt contains much of a free acid, the precipitate caused by sulphuric acid is a little retarded, but nevertheless it appears after a short time. It is only when the solution contains extremely minute traces of a baryta-salt that sulphuric acid does not immediately manifest the white precipitate in question, otherwise it is instantaneous.

* CHROMATE and BICHROMATE OF POTASH produce in solutions of barytic salts, a yellow precipitate of chromate of baryta soluble in an excess of nitric acid.

HYDROFLUOSILICIC ACID produces, after a short time, a crystalline precipitate of silicofluoride of barium, which is almost entirely insoluble in free muriatic and nitric acids.

* PERCHLORIC acid does not produce any precipitate in solutions of baryta salts.

Solution of POTASH poured in concentrated solutions of barytic salts forms a bulky precipitate of hydrate of baryta, which the addition of a great quantity of water almost entirely dissolves, provided the potash made use of be free from carbonic acid. In the course of a little time the liquid absorbs carbonic acid from the air, and at first a film and then a precipitate of carbonate of baryta takes place.

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[1] Anhydrous baryta, as well as hydrate of baryta, is very soluble in wood spirit. —E. PELIGOT.

[2] Hydrate of baryta fuses at a somewhat high temperature in its water of crystallization, which gradually evaporates, so that ultimately a white powder remains; at a higher temperature, however, this powder fuses also, and has the appearance of fused potash.—ED.

AMMONIA does not produce any precipitate in solutions of barytic salts, yet if ammonia be poured in the solution of one of these salts after standing for some time (a few days may often be requisite) a carbonate of baryta is produced owing to the absorption of carbonic acid from the air; this carbonate of baryta is deposited in the form of crystalline grains, resembling sand, and which firmly adhere to the sides of the glass, and which effervesce and disengage carbonic acid when a free acid is poured upon them. When the carbonate of baryta has completely fallen down, the liquid contains no more baryta in solution, provided always a sufficient quantity of ammonia has been added.

A solution of CARBONATE OF POTASH produces in solutions of barytic salts a white precipitate of carbonate of baryta, soluble with effervescence in acids if at all abundant, for when the quantity is very small, no effervescence takes place, because in such a case the carbonic acid disengaged remains dissolved in the liquid.

A solution of BICARBONATE OF POTASH determines also in solutions of barytic salts a white precipitate, which is only sparingly soluble in a great quantity of water. This precipitate is soluble in free acids, causing at the same time a strong effervescence.

A solution of CARBONATE OF AMMONIA poured in solutions of barytic salts produces a white precipitate of carbonate of baryta.

A solution of PHOSPHATE OF SODA produces in solutions of barytic salts, a white precipitate of phosphate of baryta, which an addition of ammonia does not increase, but which is soluble in free muriatic and nitric acids.

A solution of OXALIC ACID or of BINOXALATE OF POTASH does not yield any precipitate even in moderately concentrated solutions of neutral barytic salts. It is only in very strong solutions that a precipitate of oxalate of baryta is produced, and even then some time must elapse before it is formed. But when ammonia is added, a white precipitate of oxalate of baryta is thrown down, though even then, if the solution be very dilute, no precipitate is produced[1].

A solution of neutral SUCCINATE OF AMMONIA immediately determines the formation of a precipitate of succinate of baryta in concentrated neutral solutions of barytic salts; but when they are dilute the precipitate falls only after standing for some time. This precipitate is soluble in acids[2].

* IODATE OF SODA dissolved in cold water[3] so as to obtain a concentrated solution of the salt, determines an immediate white precipitate of iodate of baryta in barytic solutions.

HYDROSULPHURET OF AMMONIA (*sulfhydrate ammonique*) does not form any precipitate in solutions of barytic salts.

* A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate of potash*—(*cyanure ferrosopotassique*), after some standing produces a precipitate in moderately concentrated, but not in dilute solutions of barytic salts. This precipitate has a feeble yellowish-white colour, and when the two liquids are left for some time to react upon each other, crystals are deposited against the sides of the vessel. When the solution of the barytic salt is very concentrated the precipitate is promptly formed, and is a double combination of ferro-cyanuret of potassium, and of ferro-cyanuret of barium.

* A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash* — (*cyanure ferricopotassique*), does not produce any precipitate even in concentrated solutions of barytic salts.

Amongst the barytic salts soluble in water, resulting from the combination of that base with inorganic acids, the chloride is the only one which can be submitted to a red heat in contact with the air, without undergoing decomposition.

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[1] Strontian and lime are likewise precipitated by oxalate of ammonia; therefore the absence of these two earths should be ascertained before testing for baryta.—ED.

[2] This precipitate of succinate of baryta is partly pulverulent and partly crystalline.—ED.

[3] 100 parts of water at 60° dissolve 7·3 of iodate of soda.—BRANDE.

The neutral solutions of barytic salts do not react upon litmus paper. Sulphuret of barium, however, restores the blue colour to reddened litmus paper.

* Barytic salts reduced to powder, and upon which alcohol is poured, communicate a feeble greenish-yellow tinge to its flame.

Baryta forms with most acids—for example, sulphuric, phosphoric, arsenic, boracic, carbonic acids, &c.—salts which are insoluble, or almost so, in water; nearly all, however, are soluble in free muriatic or nitric acids, except sulphate of baryta, which is insoluble in them. Wherefore the presence of baryta may be detected in these acid solutions by the precipitate which diluted sulphuric acid forms in them. It is owing to this property that baryta cannot be mistaken for any other base, except strontia, and perhaps lime and protoxyde of lead. The barytic salts, which are insoluble in water, are not decomposed by a red heat.

In order to detect baryta in sulphate of baryta, water is to be poured upon a small quantity of the pulverized salt, and the whole is to be heated to ebullition, in order to ascertain whether the powder is perfectly insoluble in that liquid; it is then to be boiled with a solution of carbonate of potash or of soda, and then the liquor is to be filtered; muriatic acid is to be poured upon the portion which, after boiling, has not dissolved, and dilute sulphuric acid being added to this filtered solution, a precipitate of sulphate of baryta is produced. It will be shown further on, how sulphate of baryta may be distinguished from sulphate of strontia, which otherwise behaves exactly as sulphate of baryta when boiled with a solution of an alkaline carbonate.

The BLOW-PIPE does not furnish any characteristic reaction by which baryta or its salts can be distinguished from other substances.

* Yet, before the blow-pipe, sulphate of baryta can be

distinguished from other white precipitates, because when mixed with fluor spar it fuses easily upon charcoal in a limpid glass, which, on cooling, forms a white enamel. Sulphate of baryta, however, shares this property with sulphate of strontia and sulphate of lime[1].

Solutions of barytic salts may be distinguished from those of alkaline salts, because solution of carbonate of potash, and dilute sulphuric acid, produce white precipitates in it.

When barytic salts are contained in solutions with much organic substance, dilute sulphuric acid produces a white precipitate of sulphate of baryta, even in deeply coloured liquids, provided only they be previously acidulated with muriatic or nitric acids. In order to ascertain fully the presence of baryta in the precipitate thus obtained, it is to be treated in the manner which has been indicated just above. If it be requisite to discover the presence of baryta in pasty or solid substances, they are to be digested in water, rendered slightly acid by nitric acid; the liquor is then to be filtered, and dilute sulphuric acid is to be poured therein. When, on the contrary, the sulphate of baryta is mixed with organic substances in either the pasty or in the solid state, which are not susceptible of being dissolved in pure water, the best method is to heat the whole mass gradually and carefully in a hessian crucible, and then to urge the fire so that the carbon of the organic matter reacting on the sulphate of baryta, will convert it into sulphuret of barium: a temperature approaching a white heat is necessary to operate that effect. When the mass has cooled, it is to be boiled with water, and the solution is to be decomposed by muriatic acid. It is then very easy to detect the presence of baryta by means of diluted sulphuric acid. When the organic substances with which the sulphate of baryta is mixed are soluble in water, they may be separated by means of that solvent, and then the residuum is to be treated as we have just said [1].

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[1] With nitrate of cobalt, baryta, according to Berzelius, produces in fusing a bead which, so long as it is hot, presents a brown red or brick-red colour, or else a rusty yellow, according to the dose of the nitrate. On cooling, it loses its colour, which it reassumes by being again fused; and by exposure to the air it is soon reduced into a powder of a clear grey colour, whilst strontia with the solution of cobalt developes a black or grey black colour, and does not fuse like baryta. Lime being treated by solution of cobalt gives a black or dark grey mass, which is infusible. —ED.

6. STRONTIA, StrO.

PURE strontia resembles baryta very much, and the same remark applies to the hydrate of that base. There is, however, this difference, that it is less soluble in water than hydrate of baryta [2], owing to which its aqueous solution has a less caustic taste; but in other respects the solutions of these two hydrates react very nearly in the same manner.

Dilute SULPHURIC ACID and solutions of SULPHATES produce in solutions of salts of strontia a white precipitate of sulphate of strontia, which is insoluble in dilute free acids; even a small quantity of a salt of strontia is sufficient to produce this reaction. This white precipitate, however, appears only after a certain time, especially if the liquid contain much of a free acid. Sulphate of strontia is not so insoluble in water as sulphate of baryta. When sulphuric acid is poured in the solution of a salt of strontia, but without precipitating it completely, that is to say, so that a certain quantity of the salt remains undecomposed, and if the whole be left undisturbed for a long time before filtering it, a solution of a barytic salt poured in the clear and filtered solution produces an inconsiderable white precipitate of sulphate of baryta.

* A solution of CHROMATE OF POTASH does not immediately

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[1] Instead of dilute sulphuric acid, solution of sulphate of lime is often a better test for baryta, because by its means a sulphate of baryta is thrown down all the same; but by this re-agent, the doubt as to whether the precipitate is a sulphate of lime is avoided. Sulphate of lime, according to Mr. Taylor, may also be replaced by a saturated solution of sulphate of strontia, and forms a good test for distinguishing baryta from strontia. If a pretty large quantity of a saturated aqueous solution of sulphate of strontia be poured in a solution of a barytic salt, a white precipitate of sulphate of baryta will fall down. It is only necessary that the barytic solutions to be tested should be neutral.—ED.

[2] Hydrate of strontia dissolves in about 160 parts of water at 60°; boiling water dissolves it more abundantly, and deposits, on cooling, crystals in the form of needles or of thin quadrangular tables.—BRANDE. Hydrate of baryta dissolves in 20 parts of cold and 3 of boiling water.—DAVY.

react upon the solution of a salt of strontia, but after some time a precipitate of chromate of strontia is formed, which is easily soluble in nitric acid. A solution of BICHROMATE OF POTASH does not produce any precipitate in salts of strontia.

HYDROFLUOSILICIC ACID does not form any precipitate, even after a long time, in solutions of salts of strontia[1].

* PERCHLORIC ACID produces nothing either.

Solutions of POTASH, AMMONIA, CARBONATE, and BICARBONATE OF POTASH, CARBONATE OF AMMONIA, and PHOSPHATE OF SODA behave with salts of strontia in the same manner as with salts of baryta[2].

A solution of OXALIC ACID or of BINOXALATE OF POTASH does not immediately disturb the neutral solution of a strontia-salt when very dilute, but after some time it becomes turbid, and much more rapidly than in the dilute solution of a barytic salt. The precipitate which is formed is an oxalate of strontia, which is rendered much more abundant when ammonia is added. If the solution of the strontia-salt is so dilute that oxalic acid does not produce an immediate precipitate, it is instantly formed upon adding ammonia[3].

A solution of neutral SUCCINATE OF AMMONIA does not determine any precipitate in solutions of neutral salts of strontia, yet if the latter be very concentrated, a precipitate of succinate of strontia is produced, not immediately, but after a certain time. This precipitate is soluble in acids. By this we are enabled to distinguish solutions of strontia salts from those of baryta[4].

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[1] This acid affords therefore a good means of separating strontia from baryta, for the latter is precipitated by hydrofluosilicic acid, whilst it (the acid) forms with strontia a salt which is most readily soluble in a slight excess of acid.—ED.

[2] Carbonate of soda produces also the same reaction with salts of strontia as with those of baryta.—ED.

[3] It has been said in note 1, page 28, that baryta produces also a precipitate with oxalate of ammonia; hence the necessity of ascertaining the absence of this base before testing for strontian. This may be done by testing with a large quantity of sulphate of strontia before testing with oxalate of ammonia, which, if a precipitate is produced, indicates the presence of baryta.—ED.

[4] Succinate of strontia forms very small crystalline grains, which require a very great quantity of water for solution.—ED.

* IODATE OF SODA dissolved in cold water so as to obtain a concentrated solution, produces in strong solutions of salts of strontia an immediate precipitate of iodate of strontia; in dilute solutions the precipitate requires some time to show itself[1].

HYDROSULPHURET OF AMMONIA does not produce any precipitate in solutions of strontia salts.

* A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate of potash*—(*cyanure ferrosopotassique*) does not determine any precipitate even in strong solutions of strontian salts; and when they are as much concentrated as possible, even then the turbidness produced is quite insignificant, and only appears after a long time; this character may well serve to distinguish solutions of salts of strontia from those of baryta, lime, and magnesia [all of which produce a precipitate with this re-agent.—ED.]

A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash*—(*cyanure ferricopotassique*) does not precipitate salts of strontia from their solutions.

The strontia salts, which are soluble, behave like the barytic salts under the influence of a red heat.

Their reaction upon litmus paper is the same.

If salts of strontia be dissolved in aqueous alcohol, or if, when not soluble in this menstruum, it be poured upon this salt previously pulverized, the alcohol will burn with a carmine red flame, when set fire to. The colour of the flame becomes more intense when the whole is stirred about, or when it is nearly all burnt out, or when the alcoholic liquor is boiling; in this latter case especially, the colour is the most intense. * This character establishes quite a distinctive difference between strontian and barytic salts. The addition of a salt of baryta to the salt of strontia does not prevent the production of the red flame in question, but it gives it another tint analogous to that which is given by the salts of lime. The addition of a salt of soda modifies also that colour, and when there is a pretty large quantity of it, completely supersedes it, and nothing but the yellow colour appears[1].

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[1] Iodate of strontia is soluble in 4 parts of cold and 1¼ of hot water.—BERZELIUS.

Strontia forms salts insoluble or sparingly soluble in water with most acids, which by their combination with baryta form salts of the same nature. These salts, like those of baryta, are soluble in free muriatic or nitric acids, except sulphate of strontia, which (like sulphate of baryta) is insoluble in acids[2]. It is, therefore, easy to detect the presence of strontia in acid solutions, by means of dilute sulphuric acid. In order to distinguish the sulphate of strontia so produced from sulphate of baryta, which it closely resembles, it is necessary to decompose it by boiling it with a solution of carbonate of potash or of soda, and the insoluble residuum is to be treated by muriatic acid; the acid liquor is then to be diluted and filtered, and hydrofluosilicic acid being poured in it, if a precipitate is thereby produced sulphate of baryta is known to be present; if, on the contrary, this re-agent does not produce any precipitate, we may be certain that the combination under examination was composed of sulphate of strontia[3]. Another method which may be employed conjointly, consists in evaporating to dryness the filtered muriatic acid solution of the residuum, and pouring some alcohol upon this residuum, when upon setting it on fire its flame will assume a beautiful carmine red colour, characteristic of strontia[4].

The blow-pipe can detect the presence of strontia in a satisfactory manner only in some of the salts of that base. Fragments of crystals of sulphate of strontia held with platinum forceps at the point of the interior flame continue bubbling for a long time, and then impart a sensible but feeble red colour to the exterior flame; this colour cannot well be seen by daylight. If chloride of strontium be heated in the same manner on the bent end of a platinum wire, the flame at first assumes a deep carmine red colour, but as soon as the salt is fused the colouring vanishes altogether. Thus can chloride of strontium be distinguished from chloride of lithium. When chloride of strontium contains chloride of barium, the latter prevents the development of the red carmine colour. Sulphate of strontia heated with fluor-spar, upon charcoal, by the blow-pipe, is easily fused into a bead, which, by cooling, forms a white enamel.

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[1] Instead of alcohol, well rectified wood-naphtha produces exactly the same phenomena.—Ed.

[2] Sulphate of strontia is not altogether insoluble in water. According to Berzelius, 3840 parts of water (hot) may dissolve 1 of sulphate of strontia, but like sulphate of baryta, it is soluble in concentrated boiling sulphuric acid.—Ed.

[3] Sulphate of lime, which is a very sparingly soluble salt, and the solution of which is consequently very dilute, may serve also as a means of distinguishing salts of baryta from those of strontia. This solution of sulphate of lime will immediately produce a precipitate in solutions of salts of baryta, because it will form sulphate of baryta, which is quite insoluble; whilst in solutions of salts of strontia, no precipitate appears, at least immediately, because sulphate of strontia is, as we have seen, slightly soluble.—Ed.

[4] The absence of lime, which gives the same colour, must be previously ascertained.—Ed.

Strontia in salts of that base is recognised and distinguished from the alkaline salts by the same reactions which characterise baryta. It differs from baryta more especially, by the deportment of the latter substance with hydrofluosilicic acid; and by this, that alcohol being poured upon baryta-salts, they give no red colour to its flame[1].

When strontia is mixed with organic substances its presence may be detected by the same means which have been recommended for the detection of baryta in like mixtures.

7. LIME, CaO.

PURE lime is white, and crumbles easily between the fingers. When water is poured upon it, it becomes very hot[2], and falls into a white powder, the bulk of which is greatly superior to that of the lime which produced it. This powder is a hydrate of lime. If more water be now added to this hydrate, a milky mixture is the result. A very considerable quantity of water is requisite to dissolve a very small portion of hydrate of lime. The solution thus obtained has a feebly caustic taste, and restores the blue colour of reddened litmus paper. It strongly attracts the carbonic acid of the air, and its surface thus becomes covered with a film of insoluble carbonate of lime, which, after some time, is gradually deposited at the bottom of the vessel, and this film is renewed after each subsidence until the whole of the lime contained in the solution has fallen down in the state of carbonate[1]. Pure lime and its hydrate are both infusible.

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[1] In general, to distinguish strontia from baryta, it is customary to convert them both into chlorides by any appropriate method as has been described, evaporating the chloride solution to dryness, and pouring pure anhydrous or absolute alcohol upon the residuum.—Chloride of strontium dissolves in 24 parts of cold and 19 of boiling alcohol, whilst chloride of barium is almost insoluble in it. According to Graham, alcohol dissolves only $\frac{1}{400}$ of its weight.—ED.

[2] According to Pelletier, when this is performed in the dark, light is emitted. A match tipped with sulphur, and gunpowder may be ignited by the heat thus evolved, and even wood may be set on fire by slaking lime upon it.—ED.

Dilute SULPHURIC ACID and solutions of sulphates do not produce any precipitate in dilute solutions of lime salts. If the solution of the salt of lime be less dilute a precipitate of sulphate of lime is produced by the above re-agents, if not immediately, at least after a certain time. In concentrated solutions of salts of lime, sulphuric acid produces an immediate precipitate of sulphate of lime, which is much more bulky than the sulphate of strontia or of baryta, produced by the same means, in the respective solutions of these bases, and which is not sensibly dissolved by dilute muriatic or nitric acid. If sulphuric acid has been poured in the solution of the salt of lime in an insufficient quantity, so that a portion of the salt of lime remains undecomposed, and if the solution be then left at rest for a long time before filtering it, solutions of strontian or of barytic salts, produce in the clear filtered solution a precipitate of sulphate of strontia or of sulphate of baryta.

* SULPHATE OF POTASH dissolved in cold water does not produce, at least immediately, any precipitate in even very concentrated solutions of neutral salts of lime, and in dilute ones none is produced either, though the two mixed liquids be left to react on

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[1] This phenomenon takes place also with the aqueous solutions of baryta and of strontia.—ED.

each other for a long time; and as this solution of sulphate of potash produces an immediate precipitate in solutions of barytic salts, it should be preferred to dilute sulphuric acid, unless the acid be of a known strength, for the purpose of distinguishing baryta from lime [1].

* A concentrated solution of SULPHATE OF LIME is a better re-agent than sulphate of potash to distinguish barytic and strontian salts from those of lime. In effect it never can produce a precipitate in solutions of salts of lime however concentrated they may be, whilst it immediately forms one in solutions of barytic and strontian salts. True, that when the solutions of strontian salts are not concentrated, the precipitate of sulphate of strontia does not always take place immediately, but after some time it is always rendered manifest.

* Solutions of CHROMATE and of BICHROMATE of potash do not produce any precipitate in solutions of lime salts.

HYDROFLUOSILICIC ACID and PERCHLORIC ACID do not determine any precipitate in solutions of lime salts.

Solutions of POTASH, AMMONIA, CARBONATE and BICARBONATE OF POTASH, CARBONATE OF AMMONIA, and of PHOSPHATE OF SODA, behave with lime salt solutions as with those of baryta.

A solution of OXALIC ACID, or of BINOXALATE OF POTASH, produce, even in very dilute neutral solutions of salts of lime, a white precipitate of oxalate of lime, which augments by standing, and especially by the addition of a sufficient quantity of ammonia to saturate the free acid [2]. This precipitate is very soluble in free muriatic and nitric acids, but not much so in even concentrated acetic acid. If in a solution of a barytic, or of a strontian salt, an insufficient quantity of solution of oxalic acid, or of binoxalate of potash, be poured so as to leave in the liquid an excess of the barytic, or of the strontian salt, and if the whole be then left at rest until the precipitate formed has ceased to increase, a fresh precipitate of oxalate of lime may still be obtained by pouring the solution of a salt of lime in the filtered liquid. By this method can a soluble salt of baryta, or of strontia, be distinguished from a salt of lime[1].

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[1] Sulphate of lime answers this purpose still better; and sulphate of strontia is well adapted to distinguishing strontia from both lime and baryta. (See note 1, page 29.)—ED.

[2] Oxalate of ammonia may at once be used instead of oxalate of potash; but this salt, or its production from the addition of ammonia subsequently to the use of oxalic acid, considerably exalts the delicacy of the test, for, by this means, according to M. Lassaigne, $\frac{1}{400000}$ of lime can be detected.—ED.

A solution of neutral SUCCINATE OF AMMONIA does not determine any precipitate in neutral solutions of lime salts. When these solutions are very concentrated, a formation of crystals of succinate of ammonia takes place after standing for a long time.

* IODATE OF SODA dissolved in cold water produces a crystalline precipitate of iodate of lime in solutions of lime salts, but these solutions must be very concentrated, and the precipitate requires some time to become manifest.

HYDROSULPHURET OF AMMONIA does not produce any precipitate in lime-salts solutions.

* A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate of potash*—(*cyanure ferrosopotassique*) does not produce any precipitate in very dilute solutions of salts of lime, but in more concentrated solutions a white precipitate, which is a double combination of ferrocyanuret of potassium (yellow prussiate of potash), and of ferrocyanuret of calcium, is thrown down after some time. In those solutions which are still more concentrated the precipitate is immediately produced, and in both cases the precipitate augments by standing. It is white and soluble in muriatic acid.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash*—does not produce any precipitate in solutions of salts of lime.

The soluble salts of lime behave in the same manner as the soluble salts of baryta, when exposed to a red heat.

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[1] We have given in note 1, page 29, other means of effecting the same object. See also note 1, page 28. But the object being to ascertain whether baryta and strontia be absent, because these two bases yield also a precipitate with oxalate of ammonia, a portion may likewise be first tested with the solution of a sulphate, for which a saturated solution of sulphate of lime is perhaps preferable, before testing with oxalate of ammonia.—ED.

Their solutions react in the same manner upon litmus paper.

If alcohol be poured upon the soluble salts of lime and ignited, it burns with a red flame, which very much resembles that which the salts of strontia communicate to the flame of alcohol. This character distinguishes lime salts very well from barytic salts, but not from salts of strontia.

Lime forms insoluble or sparingly soluble salts, with the acids which produce salts of a similar composition with baryta and strontia, and these salts are likewise soluble in muriatic and in nitric acids; yet sulphate of lime is an exception, and is sparingly soluble in those acids. Sulphuric acid is a means of detecting lime in the acid solutions of lime-salts which are not too dilute, for this acid produces a precipitate if not immediately at least after some time; its determination is singularly accelerated by diluting the liquid with alcohol, because sulphate of lime is insoluble in even aqueous alcohol. For distinguishing the sulphate of lime thus precipitated from sulphate of baryta, and from sulphate of strontia, proceed as follows:—Wash the precipitate well, and boil it with a great quantity of water; filter the liquor, and divide this filtered liquor into two portions. In one of them pour a solution of chloride of barium, and in the other a solution of an oxalate. If a white precipitate is formed in both portions, and if the precipitate formed in the first portion be insoluble in muriatic acid, the base of the sulphate is lime[1].

There are but few salts of lime in which the BLOW-PIPE can conclusively detect the presence of that earth. The method employed is, however, the same as is resorted to for detecting strontia in salts of that base. In effect, chloride of calcium behaves like chloride of strontium when heated upon the bent end of a platinum wire, yet the flame is less intensely carmine-red than that given by chloride of strontium, but in both, when the salt is fused, the flame no longer shows any trace of colour. If chloride of calcium contains the least quantity of chloride of barium, its presence prevents the carmine colouring of the flame. Pure lime and carbonate of lime are exceedingly luminous under the action of the blow-pipe.

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[1] The first precipitate is sulphate of baryta, insoluble in muriatic and nitric acid; the second is oxalate of lime, which is very soluble in these two acids. Yet we must remember that sulphate of strontia is a little soluble in water, and its solution gives a precipitate with chloride of barium and with oxalate of ammonia.—ED.

* Sulphate of lime heated with fluorspar melts into a bead, which forms a white enamel on cooling[1].

Solutions of lime-salts may be distinguished from those of the alkaline salts by the same characters which establish a difference between the alkaline salts and those of baryta. They differ from baryta by their behaviour with both hydrofluosilicic acid and with a solution of sulphate of lime, and from strontia by their behaviour with a solution of sulphate of lime.

When the solution of a lime-salt is mixed with *much organic matter* which gives it a very deep colour, in order to detect the presence of lime, the solution is to be mixed with a solution of commercial binoxalate of potash, and then a little ammonia is to be added. But when the solution is acid, or strongly alkaline, it should first be rendered neutral, in the first case by means of ammonia, in the second by means of muriatic acid. A precipitate of oxalate of lime then takes place, which at times is deeply coloured. This salt is to be dried, and exposed to a red heat, which converts it into carbonate of lime. The residuum is next to be dissolved in muriatic acid, and the presence of lime in this solution can then be positively ascertained. If the lime or a salt of lime be mixed with organic substances in the solid or in the pasty state, it is best to treat the mass with water acidulated with nitric acid. By filtering this liquor, the presence of lime can then be easily detected in the way we have said. When, on the contrary, sulphate of lime is mixed with organic substances, in the solid or in the pasty state, but which are insoluble in pure water, the mass must be treated in the manner indicated (page 28) for sulphate of baryta in parallel cases; * but instead of boiling with water the mass which has been made red hot, it is to be treated immediately by muriatic acid, because the sulphuret of calcium produced is very sparingly soluble in water.

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[1] M. Plattner has given the following method of detecting lime in barytic and strontian salts. The pure salts fuse with salt of soda upon platinum foil, and give a clear flux; but if they contain lime, it remains undissolved. Putting the fused assay upon charcoal and continuing the blast, the clear flux penetrates the charcoal and the lime remains at the surface.—*Journal für pr. Chemie.*—Ed.

8. MAGNESIA, MgO.

In the pure state, magnesia is a white powder which is very sparingly soluble in water[1], and infusible. If a little of the powder be spread upon reddened litmus paper, and moistened thereon, it restores the blue colour of the paper. When a small quantity of water is poured upon it, it does not become hot.

Sulphuric acid does not produce any precipitate in concentrated solutions of salts of magnesia.

Hydrofluosilicic acid and perchloric acid do not produce any precipitate either.

A solution of potash determines in solutions of neutral salts of magnesia a bulky, flocculent precipitate of hydrate of magnesia, which remains permanent on diluting the liquor with water. If the solution of magnesia had previously been mixed with a solution of muriate of ammonia (*chlorure ammonique*), and potash be then added, the precipitate is much less considerable. When, potash being poured in a magnesian solution, a solution of muriate of ammonia is further added, the precipitate of hydrate of magnesia produced at first by the potash almost entirely disappears. But if the whole be made to boil, the precipitate of hydrate of magnesia always becomes manifest if potash be in excess.

Ammonia produces in neutral magnesian solutions a bulky precipitate of hydrate of magnesia, which disappears almost entirely by the addition of a solution of muriate of ammonia, or of any other ammoniacal salt. If to a neutral solution of magnesia, one of muriate of ammonia be added, and then if ammonia be poured in the mixture, no precipitate is formed, provided a sufficient quantity of muriate of ammonia has been employed. If the solution of the magnesian salt is not neutral, but contains a free acid, the ammonia which is added in excess does not produce any precipitate either, provided the free acid be in sufficient quantity[1].

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[1] According to Berzelius 5142 parts of water at 60° are requisite to dissolve one of magnesia.—Ed.

A solution of CARBONATE OF POTASH determines in neutral magnesian solutions a bulky precipitate of subcarbonate of magnesia, which disappears completely by the further addition of a solution of muriate of ammonia. *Carbonate of potash* does not determine any precipitate when the solution of muriate of ammonia is mixed with the liquor before testing with carbonate of potash. If, however, in either case, the liquor is made to boil, provided carbonate of potash be in sufficient quantity, a bulky precipitate appears. When a solution of a magnesian salt contains much of a free acid, and is not too concentrated, carbonate of potash does not produce any precipitate in it, yet by boiling it, a precipitate of subcarbonate of magnesia is formed.

A solution of BICARBONATE OF POTASH does not produce any precipitate, even in concentrated solutions of neutral magnesian salts. But if the mixture be made to boil, a disengagement of carbonic acid takes place, and a precipitate of subcarbonate of magnesia is produced.

A solution of CARBONATE OF AMMONIA does not produce any precipitate in magnesian solutions, but if the whole be made to boil, a precipitate of subcarbonate of magnesia takes place, which, however, disappears also by the addition of a solution of muriate of ammonia.

A solution of PHOSPHATE OF SODA produces a precipitate of phosphate of magnesia in concentrated neutral magnesian solutions. When these solutions are somewhat dilute, no precipitate appears if the mixture be made in the cold way, but if the whole be boiled, a precipitate of phosphate of magnesia may be observed, which does not disappear on cooling. When a solution of phosphate of soda has been mixed with a neutral solution of magnesia, if the mixture be so dilute as not to produce any precipitate when cold, a precipitate of ammonio-magnesian subphosphate is immediately produced by the addition of ammonia or of carbonate of ammonia. * The presence of even a pretty considerable quantity of muriate of ammonia or of other ammoniacal salts does not interfere in the least with the production of this precipitate.

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[1] This of course is owing to the ammonia forming with the free acid an ammoniacal salt which interferes with or prevents the precipitation of the magnesia.—ED.

Solutions of OXALIC ACID or of BINOXALATE OF POTASH do not produce any precipitate in neutral magnesian solutions. If the quantity of the solution of oxalic acid or of oxalate be not very considerable, the addition of ammonia produces a precipitate, even though the solution may have previously been diluted with a large quantity of water. But if a great quantity of solution of oxalic acid or of oxalate has been poured in the magnesian solution, or if the solution of magnesian salt was not neutral, but contained a free acid, an excess of ammonia produces no precipitate or turbidness in even very concentrated solutions, because there is then a sufficient quantity of ammoniacal salt produced to prevent the precipitation of the magnesia.

HYDROSULPHURET OF AMMONIA (*sulfydrate-ammonique*) does not determine any precipitate in magnesian solutions unless they be extremely concentrated. When this re-agent produces one in neutral magnesian solutions, it is a proof that it contains, as is very often the case, a great deal of free ammonia to which the precipitate of hydrate of magnesia is due.

* A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate of potash*—(*cyanure ferrosopotassique*) determines, after some time, in solutions of magnesian salts, an abundant white precipitate, which is a double combination of ferrocyanuret of potash and of ferrocyanuret of magnesia.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate* (*cyanure ferrico-potassique*) does not produce any precipitate in solutions of magnesian salts.

Among the salts of magnesia which are soluble in water, sulphate of magnesia is the only one which can bear a red heat in contact with the air without undergoing decomposition.

Solutions of neutral magnesian salts do not react upon litmus paper.

Magnesia forms with a great number of acids salts which are insoluble or sparingly soluble in water, such are, for example, the phosphates, arseniates, carbonates and borates. All these salts are soluble in either sulphuric or muriatic acids. Some magnesian super-salts, after having been exposed to a red heat, can no longer be dissolved in these acids, unless they be previously boiled in concentrated sulphuric acid, such, for example, is the case with superphosphate of magnesia. In order to detect the presence of magnesia in acid solutions of magnesian salts, it is often necessary to boil them for a pretty long time with an excess of a solution of potash; magnesia is then precipitated in the state of a hydrate, whilst the acid with which it was combined, and that which was made use of to dissolve it, unite with the potash and remain in the solution. The well-washed precipitate may then be examined with the blow-pipe or else dissolved in an acid; for example, in muriatic acid, or in dilute sulphuric acid, in which solution magnesia may then be easily recognised.

Magnesian salts may also be detected in the following manner:—A small piece is to be heated red hot upon charcoal by means of the *blow-pipe,* and immediately moistened with nitrate of cobalt; then it is to be heated anew and strongly. The piece so treated assumes then a *characteristic* pale red of flesh colour in those parts which have imbibed nitrate of cobalt, an effect which is not manifested in substances which contain no magnesia[1]. Pure magnesia and carbonate of magnesia mixed into a paste with water, spread upon charcoal and there made red hot, manifest also a red or flesh colour with nitrate of cobalt as above. The presence of metallic oxydes, of alkalies, and of earths, prevents the reaction of the salt of cobalt; silicic acid, on the contrary, does not interfere with it.

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[1] This flesh colour is, however, very weak, and can be well perceived only after the complete cooling of the piece.—Ed.

Solutions of neutral salts of magnesia are distinguished from those of alkaline salts, because ammonia and a solution of carbonate of potash produce white precipitates in them; they differ from solutions of baryta, strontia, and lime, because ammonia does not produce any precipitate in these three earths.

Acid solutions of magnesia are distinguished from those of potash, soda, and ammonia-salts, because, after having been supersaturated with ammonia, a solution of phosphate of soda produces a white precipitate[1]. They are distinguished from solution of salts of lithia because an excess of potash produces in the magnesian solutions a precipitate, especially by boiling the whole;—from solutions of salts of baryta and strontia, because dilute sulphuric acid does not produce any precipitate;—lastly, from solutions of salts of lime by their behaviour with solution of oxalic acid[2].

The presence of non-volatile *organic substances* may often prevent or at least interfere with the precipitation of magnesia by alkalies; yet when the proportion of magnesia is small, and that of organic substances large, magnesia is nevertheless precipitated from such solutions by phosphate of soda with addition of ammonia[3].

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[1] Phosphate of ammonia (according to M. Lassaigne) can detect $\frac{1}{200000}$ of magnesia, but to the magnesian solution a quantity of a concentrated solution of an ammoniacal salt equal to its own weight must be added. The precipitate of ammonio-magnesian subphosphate, dissolves readily in acids.—Ed.

[2] M. Döbereiner (*Journ. für pr. Chemie*, xvi.), indicates the following method to separate lime from magnesia:—These two earths are to be dissolved in muriatic acid and evaporated to dryness. The residuum is to be calcined in a platinum crucible until no more hydrochloric acid is disengaged; and pulverised chlorate of potash is to be added by small portions until all smell of chlorine has ceased. Water being now added, the chloride of calcium produced will dissolve whilst the magnesia remains insoluble. Berzelius's method to operate this separation consists in mixing the solution of chloride of calcium, which might contain chloride of magnesium with peroxide of mercury, evaporating to dryness, and igniting so as to completely expel the mercury. By lixiviating with water, the chloride of calcium is dissolved whilst the magnesia remains insoluble.—Ed.

[3] It should be recollected that baryta, strontia, and lime are likewise precipitated

9. ALUMINA, AlO_3.

PURE alumina is white, but it often has a slightly yellowish tinge, and a horny appearance when obtained by slowly drying the hydrate of alumina[1]. It is insoluble in water[2], but is easily dissolved in acids, provided it has not been previously made red hot. After it has thus been calcined, it becomes of difficult solubility, and is almost insoluble in certain acids, and then the best means of dissolving it consists in digesting it in concentrated muriatic acid diluted with a very small quantity of water, or in heating it with sulphuric acid slightly diluted.

No free acid, even hydrofluosilicic acid, produces any precipitate in solutions of alumina salts.

A solution of POTASH determines in solutions of neutral salts of alumina a bulky precipitate of hydrate of alumina, which is immediately redissolved by the addition of an excess of potash. A solution of muriate of ammonia poured in such a solution determines a precipitate of hydrate of alumina.

AMMONIA poured in solutions of salts of alumina produces a voluminous precipitate of hydrate of alumina, insoluble in an excess of ammonia. The presence of muriate of ammonia does not interfere with the formation of this precipitate, nor of that produced by the following re-agents, a character which quite distinguishes alumina salts from those of magnesia[3].

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by phosphate of soda, though the precipitate is not augmented by the addition of ammonia; and therefore the absence of these three earths should be ascertained before testing with phosphate of soda, either with or without addition of ammonia.—ED.

[1] This yellowish tinge is not inherent to alumina, but is always owing to organic substances which are mixed with it, and for which alumina has a great affinity. When this is the case, upon applying heat to it, it becomes black from their being charred.—ED.

[2] Pure alumina is absolutely insoluble in water, but it has so much affinity for that liquid, that even in the dry state it retains a great quantity of it which cannot be driven off except by igniting it.—ED.

[3] According to Gay Lussac, when alumina is precipitated by ammonia, the precipitate retains a subsulphate of alumina which cannot be decomposed by any excess of ammonia.—ED.

15.2

A solution of CARBONATE OF POTASH produces in solutions of alumina-salts a precipitate of hydrate of alumina as bulky as that produced by ammonia; this precipitate is likewise insoluble, or nearly so, in an excess of the re-agent. If the solution be concentrated, an effervescence is produced in solutions of neutral salts of alumina, owing to a disengagement of carbonic acid. If, however, a great excess of carbonate of potash be employed, no effervescence takes place, because a bicarbonate is then produced[1].

A solution of BICARBONATE OF POTASH has the same reaction, only the effervescence produced by the disengagement of carbonic acid is stronger still.

A solution of CARBONATE OF AMMONIA behaves in the same manner, and the precipitate is insoluble in an excess of the re-agent.

A solution of PHOSPHATE OF SODA produces in solutions of neutral salts of alumina a bulky precipitate of phosphate of alumina, which like the other precipitates is soluble in acids, and in a solution of potash, and the external characters of which have a great resemblance with hydrate of alumina.

A solution of OXALIC ACID, and of NEUTRAL OXALATES, does not determine any precipitate in neutral solutions of alumina.

If POTASH, or CARBONATE OF POTASH, be added to a solution of alumina, and a sufficient quantity of SULPHURIC ACID be added to the liquid, so that it should slightly predominate, crystals of alum are formed after some time, provided the alumina solution be not too diluted. When the liquor is too dilute, it must first be concentrated by evaporation, without which precaution sulphuric acid and potash will yield no crystals of alum.

* AMMONIA, likewise, yields crystals of alum in alumina solutions in the same circumstances as just related in reference to potash.

* A solution of FERROCYANURET OF POTASSIUM — *yellow*

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[1] The alumina thus precipitated by carbonate of potash is always mixed with a little potash. It is therefore well, in order to have it pure, to redissolve it in muriatic acid, and then to precipitate it again by ammonia.—ED.

prussiate—(*cyanure ferroso-potassique*) does not immediately produce a precipitate in solutions of salts of alumina, but after some time an abundant precipitate is formed, which remains for a long time in suspension.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate*—(*cyanure ferrico-potassique*) does not determine any precipitate in solutions of salts of alumina.

HYDROSULPHURET OF AMMONIA forms, in neutral solutions of alumina, a precipitate of hydrate of alumina; sulphuretted hydrogen is disengaged with effervescence when the solutions are very concentrated. This precipitate being formed of pure hydrate of alumina is soluble in a solution of potash.

A current of SULPHURETTED HYDROGEN, or a solution of that gas in water, does not determine any precipitate in neutral solutions of alumina, neither does it form one in solutions of alumina in potash.

* When alumina, or a salt of alumina, is heated red hot with an excess of carbonate of potash or of soda, the alumina displaces the carbonic acid of the alkaline carbonate, and the melted mass is completely soluble in water.

Neutral soluble salts of alumina react upon blue litmus paper, and turn it red.

The salts of alumina, which are soluble in water, are decomposed when submitted to a red heat.

Alumina forms with a great number of acids, for example, phosphoric acid, arsenic acid, &c., salts which, when neutral, are insoluble in water. When these salts have not been exposed to a red heat, they very readily dissolve in muriatic or in sulphuric acid, and likewise in solution of potash. Solutions of phosphates, arseniates, &c. of alumina in acids, and in solution of potash, behave with re-agents about the same manner as a solution of pure alumina. These salts may easily be mistaken for pure alumina; in order to distinguish them from it, it is therefore necessary to test for the acids with which it may be combined. The means of effecting this are indicated further on.

Before the *blow-pipe*, alumina, either in the pure state, or in most of its combinations, may be easily recognised, especially when these combinations are not very fusible. In effect, if a small quantity of the substance be heated upon charcoal, with a solution of nitrate of cobalt, it assumes a beautiful blue colour upon being heated again strongly in the flame of the blow-pipe; this colour is quite characteristic, and is not manifested in substances which contain no alumina. This colour can be seen to be a pure blue only by daylight, for by candle or artificial light it has a dirty *purple* appearance[1].

Solutions of salts of alumina may easily be distinguished from those of alkaline salts, because ammonia produces a precipitate in alumina solutions; from those of barytic, strontian and lime soluble salts,—because ammonia does not produce any precipitate in the three latter solutions,—and because sulphuric acid produces in them also a precipitate, whilst none is formed by sulphuric acid in salts of alumina: the solutions of salts of lime, however, in order to produce a precipitate with sulphuric acid, must not be too dilute; and, lastly, they may be distinguished from those of magnesian salts by their behaviour with solutions of potash and of muriate of ammonia.

In solutions of alumina, which contain much organic matter, especially such as cannot be volatilised by heat without being decomposed or destroyed, and which therefore leave a copious residuum of charcoal, it often happens that the presence of alumina cannot be ascertained by means of the ordinary re-agents, even though the liquid be almost colourless. Ammonia and solutions of carbonate of potash do not produce any precipitate in such solutions, even though a very great excess of these re-agents be employed; and it is with difficulty that crystals of alum are formed in it by the addition of potash and of sulphuric acid. The presence of alumina can often be detected in solutions containing much organic matter only by evaporating the liquid to dryness, and igniting the residuum, by which means the organic substance is destroyed. After ignition the residuum is to be digested in an acid; for example, muriatic or sulphuric acids, and then alumina may be tested for in the filtered liquor with the ordinary re-agents. When alumina is contained in organic substances in the solid or in the pasty state, the organic substances must likewise be destroyed by igniting the whole, and alumina may then be tested for as above.

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[1] The blue colour can also be distinctly seen only after the mixture operated upon has cooled, and a greater dose of cobalt renders it deeper, but not less beautiful.—Ed.

10. GLUCINA GlO.

PURE glucina is white and insoluble in water. It is soluble in acids, but less easily after having been ignited.

Free acids, even hydrofluosilicic acid, do not form precipitates in glucina solutions.

POTASH produces a bulky precipitate of hydrate of glucina, which is completely soluble in an excess of potash; solution of muriate of ammonia (*chlorure ammonique*) produces a precipitate of hydrate of glucina in such a solution.

AMMONIA produces in glucina solutions a bulky precipitate of hydrate of glucina, which is insoluble in any excess of this re-agent. Solution of muriate of ammonia does not prevent the formation of this precipitate, nor of that produced by any of the following re-agents[1].

A solution of CARBONATE OF POTASH produces in glucina solutions a bulky (flocculent) precipitate of carbonate of glucina, soluble in a great excess of the re-agent.

A solution of BICARBONATE OF POTASH acts in the same way.

A solution of CARBONATE OF AMMONIA acts in the same way as carbonate of potash, only the precipitated carbonate of glucina is more easily soluble in carbonate of ammonia than in carbonate of potash. When such a solution is made to boil the carbonate of glucina falls down[1].

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[1] Potash and ammonia behave therefore with glucina exactly as with ~~potash~~, which circumstance might cause it to be confounded with alumina; but as it is perfectly soluble in carbonate of ammonia, whilst alumina is not, and does not form alum by treatment with potash and sulphuric acid, these characters are sufficient to distinguish it; neither does it yield the blue-coloured glass, before the blowpipe, with nitrate of cobalt.—ED.

A solution of PHOSPHATE OF SODA determines a bulky precipitate of phosphate of glucina in glucina solutions.

A solution of OXALIC ACID or of OXALATES does not produce any precipitate in glucina solutions.

When POTASH is poured in a glucina solution, no crystals of alum are formed by super-saturating it with sulphuric acid.

A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate*—does not immediately produce any precipitate in glucina solutions, * but, after some time, the liquid becomes gelatinous, and this gelatinous liquid assumes a blue tinge if it contains the least iron.

FERRICYANURET OF POTASSIUM—*red prussiate of potash*—does not determine any precipitate in glucina solutions.

HYDROSULPHURET OF AMMONIA produces in neutral solutions of glucina a precipitate of hydrate of glucina soluble in a solution of potash.

A solution of SULPHURETTED HYDROGEN, or a current of the gas, does not produce any precipitate in solutions of glucina.

Neutral solutions of glucina react on litmus paper and turn it red.

The glucina salts soluble in water are decomposed by the action of a red heat.

Glucina forms, with a great number of acids, salts which, in the neutral state, are insoluble in water; these salts are often, like the corresponding salts of alumina, very difficult to distinguish from pure glucina.

Glucina and most of its combinations, before the *blow-pipe*, and after having been moistened with solution of nitrate of cobalt, assume, not a blue colour (as alumina), but become deep grey or black.

Solutions of glucina are distinguished from alkaline and also from barytic, strontian, lime and magnesian solutions by the same characters which establish a difference betwixt these and the solutions of alumina. They are distinguished from the latter solutions by their behaviour with solutions of the alkaline carbonates, and especially with that of carbonate of ammonia; by their reaction with potash and sulphuric acid (no crystals of alum being produced); and lastly, when in the solid state, by their behaviour before the blow-pipe with solution of nitrate of cobalt.

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[1] This precipitate is granular, and easily falls at the bottom of the vessel. It is light and soft when dried.—ED.

* There is, according to Berzelius, a phenomenon which, for the salts of glucina, is quite characteristic; it is that when their hot solution is mixed with a hot solution of fluoride of potassium until a precipitate begins to appear, a sparingly soluble double fluoride of glucinium and potassium in small scaly crystals is deposited on cooling the mixture.

When a solution of glucina contains a great quantity of non-volatile *organic matter*, glucina is as difficult as alumina to be detected therein by means of the ordinary re-agents. It is then equally necessary to evaporate the liquor to dryness, to ignite the residuum; then to treat it by muriatic acid, and lastly to test for glucina in the acid solution.

11. THORINA, ThO.

THORINA being an extremely rare substance, I have had yet no opportunity of studying it, nor examining its behaviour with re-agents. That which I am about to say upon this substance is extracted from the memoir which Berzelius has published on that substance.

Pure thorina is colourless; after ignition it cannot be dissolved in any acid except concentrated sulphuric acid, to which an equal weight of water has been added, and yet it must be heated to operate its solution. It is useless to ignite thorina with alkalies, for such a treatment will not render it soluble in either muriatic or nitric acid, as is the case with almost all the other oxydes, which, after ignition, are insoluble in acids. Acids take up only the foreign substances with which thorina may be mixed, and upon which they have no action, except after ignition with an alkali. The hydrate of thorina when moist, on the contrary, is very easily soluble in acids; after it has been dried, its solution is more difficult and slow.

A solution of POTASH produces in solutions of thorina a gelatinous precipitate of hydrate of thorina, which, however, very soon gathers at the bottom of the vessel, and which is insoluble in an excess of the re-agent.

AMMONIA behaves in the same manner.

Solutions of CARBONATE OF POTASH and of CARBONATE OF AMMONIA determine in solutions of thorina a precipitate which is soluble in an excess of the re-agent. This solution is pretty easily effected when the solution of the carbonate is concentrated; but when it is too dilute it is difficult to dissolve it.

A solution of PHOSPHATE OF SODA forms, in a solution of thorina, a white flocculent precipitate of phosphate of thorina, insoluble in an excess of phosphoric acid.

A solution of OXALIC ACID produces a white, heavy precipitate of oxalate of thorina, insoluble in an excess of oxalic acid, and which is also very sparingly soluble in other free dilute acids.

A solution of SULPHATE OF POTASH renders solutions of thorina turbid; this turbidness is slowly manifested, but the thorina becomes entirely precipitated in the state of potassio-sulphate of thorina, provided the solution of the sulphate be concentrated and in excess.

A solution of FERROCYANURET OF POTASSIUM produces in a neutral solution of thorina a white, heavy precipitate of ferrocyanuret of thorina, soluble in acids.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate*—produces no precipitate in solutions of thorina.

HYDROSULPHURET OF AMMONIA determines a precipitate of hydrate of thorina in neutral solutions of thorina.

SULPHURETTED HYDROGEN, either liquid or gaseous, yields no precipitate in solutions of thorina.

The salts of thorina, soluble in water, are decomposed when submitted to a red heat. Several solutions of these salts, for example, that of the sulphate, are precipitated by boiling[1]; yet this re-action does not take place when bases are present, with which thorina forms double *salts*.

Solutions of thorina are distinguished from alkaline solutions as well as those of baryta, strontia, and lime, because it is precipitated by ammonia from magnesian solutions by their behaviour with ammonia and muriate of ammonia[2]; lastly, from alumina and glucina, because a solution of potash produces a precipitate which is not soluble in an excess of the re-agent.

12. YTTRIA, YO.

PURE yttria—*hydrate of yttria*—is white, and becomes of a dirty yellow colour when it has been made red hot. It is easily soluble in acids.

A solution of POTASH produces, in solutions of yttria, a white bulky precipitate of *hydrate of yttria*, which is insoluble in an excess of the re-agent.

AMMONIA behaves in the same manner.

A solution of CARBONATE OF POTASH determines, in solutions of yttria, a white bulky precipitate of carbonate of yttria, which is slightly soluble in a great excess of the re-agent.

A solution of BICARBONATE OF POTASH produces a white bulky precipitate of carbonate of yttria, which is entirely soluble in a very great excess of the re-agent.

A solution of CARBONATE OF AMMONIA behaves in the same manner; * yet a much larger quantity of this re-agent is necessary to dissolve yttria than is necessary for glucina. When yttria contains peroxyde of iron or of cerium, it is very sparingly soluble in a solution of carbonate of ammonia.

A solution of PHOSPHATE OF SODA causes, in neutral solutions of yttria, a white precipitate of phosphate of yttria, which is soluble in muriatic acid, and which is precipitated from the solution by boiling.

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[1] This property of sulphate of thorina, of being precipitated by boiling, and to be re-dissolved again entirely, though slowly, on cooling, is quite peculiar, and distinguishes it from all other oxydised bodies as yet known.—BERZELIUS.

[2] Thorina is distinguished from magnesia, because if ammonia is added to a muriatic acid solution of thorina and magnesia, the thorina is precipitated, whilst the magnesia is kept in solution by the muriate of ammonia. It is only necessary to put a sufficient quantity of muriate of ammonia.—ED.

A solution of OXALIC ACID produces in slightly acid solutions of yttria a white bulky precipitate of oxalate of yttria, which is soluble in muriatic acid.

A solution of SULPHATE OF POTASH determines, after some time, in solutions of yttria, a precipitate, which is a double sulphate of yttria and of potash, sparingly soluble, and which is completely dissolved when much water is added, but the solution of which takes place, though slowly, even though the water contains sulphate of potash in solution.

A solution of FERROCYANURET OF POTASH—*yellow prussiate*—produces a white precipitate of ferrocyanuret of yttria.

A solution of FERRICYANURET OF POTASH does not produce any precipitate.

HYDROSULPHURET OF AMMONIA produces a precipitate of hydrate of yttria in neutral solutions of yttria.

Aqueous solutions of SULPHURETTED HYDROGEN, or a current of the gas, does not produce any precipitate in solutions of yttria.

Neutral solutions of the salts of yttria redden blue litmus paper.

The salts of yttria, which are soluble in water, are decomposed when they are made red hot.

* The salts of yttria, which are insoluble in water, are often somewhat difficult to distinguish from pure yttria.

Yttria, before the BLOW-PIPE, behaves like glucina, and is not easy to distinguish from similar earths.

Solutions of yttria may be distinguished from alkaline solutions and from those of baryta, strontia, lime, and magnesia, by the same characters which establish a difference between these and solutions of alumina. From solutions of alumina and of glucina, because they yield a precipitate with solution of potash, which precipitate is insoluble in an excess of this re-agent[1];

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[1] Yttria is, according to Berzelius, particularly distinguished from glucina, because it is precipitated by ferrocyanuret of potassium; but the character which best

from solutions of thorina, because these form with sulphate of potash a double salt, which is insoluble in a saturated solution of sulphate of potash.

The presence of organic substances does not prevent yttria from being precipitated from its solution by alkalies.

13. OXYDES OF CERIUM.

1°. PROTOXYDE OF CERIUM, CeO.

(*Oxyde céreux.*)

Pure hydrate of protoxyde of cerium is white, but it becomes yellow by exposure to the air, the oxygen of which it absorbs. When it is heated to redness in contact with the air, it acquires a brick red colour, because it is converted thereby into peroxyde of cerium. It easily dissolves in acids. Hot muriatic acid almost always dissolves it with a feeble evolution of chlorine. Yet, this is a property of the peroxyde of cerium and not of the protoxyde, but it is caused in consequence of the protoxyde containing always a certain quantity of the peroxyde, by reason of the facility with which the protoxyde absorbs oxygen from the air when moist[1].

A solution of **potash** produces in solution of protoxyde of cerium a white bulky precipitate of hydrate of protoxyde of cerium, insoluble in an excess of the re-agent.

Ammonia behaves in the same manner.

Carbonate of potash determines a white voluminous precipitate of protocarbonate of cerium very sparingly soluble in an excess of the re-agent.

Solutions of **bicarbonate of potash** and of **carbonate of ammonia** behave in the same manner.

A solution of **phosphate of soda** yields a precipitate of protophosphate of cerium in neutral solutions of protoxyde of cerium.

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distinguishes it from all other earths, is, that its sulphate produces small crystals of an amethyst colour, efflorescent by heat, and remarkable by the excessive slowness with which they dissolve in water.—Ed.

[1] This property, according to Berzelius, is the cause of its never having been obtained in the anhydrous state, for all attempts to dry it are attended with its partial peroxydisement.—Ed.

A solution of OXALIC ACID produces, even in acid solutions of protoxyde of cerium, provided they do not contain too much free acid, an immediate white precipitate of oxalate of cerium, which is soluble in a large excess of muriatic acid.

A solution of SULPHATE OF POTASH poured in solutions of protoxyde of cerium, provided they be not too dilute, occasions, if not immediately, at least after a short time, a crystalline precipitate, which is a double sulphate of potash and of cerium very sparingly soluble in water, and insoluble in a solution of sulphate of potash[1] [with which it may be washed] as will be said in the second volume.

A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate of potash*—produces a white precipitate of ferrocyanuret of cerium in neutral solutions of the protoxyde.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash*—does not determine any precipitate.

HYDROSULPHURET OF AMMONIA produces in neutral solutions of protoxyde of cerium a white precipitate of protoxyde of cerium. * But if there be the least trace of iron or of cobalt the precipitate is black.

SULPHURETTED HYDROGEN in aqueous solutions, or in the gaseous state, does not produce any precipitate in solutions of protoxyde of cerium.

Neutral solutions of protoxyde of cerium redden litmus paper.

The salts of protoxyde of cerium, which are soluble in water, are decomposed by being submitted to a red heat, with the single exception of the double sulphate of cerium and of potash.

Protoxyde of cerium may be shown to exist in combinations which are not soluble in water, but this is attended with some difficulty. The best method is to dissolve these combinations in an acid, and to promote the formation of the double sulphate of cerium and potash by plunging in the liquid a crust of crystals of sulphate of potash, the double sulphate thus formed being insoluble in a solution of sulphate of potash.

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[1] By boiling this precipitate in water, according to Berzelius, it crystallises by cooling in small crystals of a red amethyst colour, which is characteristic, and may serve to separate it from other oxydes.—ED.

Before the BLOW-PIPE, protoxyde of cerium becomes converted into the sesquioxyde, which borax and the salt of phosphorus (microcosmic salt) dissolve in the exterior flame, and yield a red glass [or orange yellow] [1], the colour of which becomes weaker on cooling, so as often to entirely disappear. This colour is completely dissipated in the interior flame.

Solutions of protoxyde of cerium may be distinguished from solutions of alkalies, and from those of baryta, strontia, lime, and magnesia, by the same characters which establish a difference between these and the solutions of alumina. Protoxyde of cerium differs from alumina and from glucina by its insolubility in an excess of potash. It differs from thorina only because thorina does not assume a brick red colour like the protoxyde of cerium when submitted to a red heat, nor does it give a coloured glass, either before or after cooling (provided it contains no peroxyde of iron) when treated before the blowpipe with borax, or with microcosmic salt. Lastly, it differs from yttria by the same character, and also by the behaviour of its solutions with sulphate of potash.

Alkalies do not precipitate protoxyde of cerium from its solution, which contains non-volatile organic substances.

2°. SESQUIOXYDE OF CERIUM [Ce_2O_3].

(*Oxyde cérique.*)

SESQUIOXYDE of cerium—*peroxyde of cerium*—(*oxyde cérique*) is pulverulent, and of a brick red colour—soluble in hot muriatic acid, with disengagement of chlorine; the solution contains then a protochloride of cerium, and behaves therefore with re-agents in the same manner as the solutions of protoxyde of cerium. Even when the sesquioxyde of cerium has been dissolved by boiling it in dilute sulphuric acid, this solution behaves with re-agents in the same manner as the solutions of the protoxyde[1]. Nevertheless, the white precipitates of protoxyde of cerium have sometimes a yellow tinge[2], which is owing to a certain quantity of sesquioxyde which they contain.

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[1] With microcosmic salt, however, Berzelius says that this oxyde yields a fine red glass, but which disappears on cooling, and is as clear as water.—ED.

The French edition has the following addition by E. Peligot :—

LANTHANUM.

M. Mosander discovered, in 1839, in the mineral called *cerite* of Bastnaes, a new metal, to which he gave the name of lanthanum. Oxyde of cerium extracted from cerite by the usual method contains about two-fifths of its weight of oxyde of lanthanum, which differs but little from cerium, in which it is, as it were, hidden; hence the name given by Mosander to his new element[3].

OXYDE OF LANTHANUM [LnO].

(*Oxyde lanthanique.*)

Oxyde of lanthanum differs from oxyde of cerium, because it is soluble in weak acids, whilst oxyde of cerium is not thus acted upon; it is prepared by calcining the nitrate of cerium, which is mixed with nitrate of lanthanum, and treating the red oxyde which constitutes the mixtures of the two oxydes by nitric acid diluted with 100 parts of water.

Oxyde of lanthanum has a red brick colour. Hot water changes it into a white hydrate, which has an alkaline reaction. It displaces ammonia from its combinations and is soluble in the weakest acids; it has very decided basic properties.

Salts of lanthanum have an astringent taste, without sweetness; their crystals are ordinarily of a pink tint. Sulphate of potash does not precipitate them unless they be mixed with salts of cerium.

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[1] Because the sesquioxyde is reduced to the protoxyde of cerium.—Ed.

[2] When a solution of caustic potash is poured in the solution of a salt of peroxyde of cerium (Berzelius), a mucilaginous pale yellow precipitate of (hydrate cérique) hydrated sesquioxyde is formed, which becomes of a deep yellow colour by drying.—Ed.

[3] From λανθανειν, to hide one's self.

Sulphuret of lanthanum may be produced by strongly heating oxyde of lanthanum in the vapour of bisulphuret of carbon; it has a pale yellow colour, and decomposes water with a disengagement of sulphuretted hydrogen, and is converted into the hydrate.

Oxyde of lanthanum is not reduced by potassium; but this metal separates from chloride of lanthanum a grey powder, which is oxydised by water, with disengagement of hydrogen, and becomes at the same time converted into a white hydrate. This powder is lanthanum.

Since the publishing of his memoir, M. Mosander has announced that cerite contains a third metal, to which he refers the pink colour of the salts of lanthanum: he named it Didymum, (δίδυμοι, twin), to recall to the mind its resemblance with lanthanum, and the power with which these salts persist in their union with those of lanthanum[1].

14. ZIRCONIA [Zr_2O_3].

Hydrate of zirconia forms, like that of alumina, a mass having a slight tinge of yellow, and of a horny appearance, and which, whilst moist, readily dissolves in acids, for example, in muriatic acid, especially with the application of heat. In the dry state it is less soluble in acids. At a red heat it becomes incandescent, and after ignition the zirconia has a perfectly white colour. In that state it is insoluble in almost all acids; yet, after having been boiled for a long time with sulphuric acid[2], it becomes soluble in boiling water. It is infusible and very hard.

A solution of potash produces, in solutions of salts of zirconia, like in those of salts of alumina, a bulky precipitate of hydrate of zirconia, insoluble in an excess of the re-agent.

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[1] According to Hermann, a white flocculent precipitate is produced in solutions of oxyde of lanthanum by *fluoride* of sodium. Phosphoric and oxalic acids yield also white precipitates, which are slightly soluble in an excess of the acid. Ferrocyanuret of potassium gives a white precipitate.—Ed.

[2] According to Berzelius, it should be carefully and finely pulverised before putting it in the sulphuric acid, in order to promote its solution; and the sulphuric acid should be diluted with about its own weight of water. The solution should be evaporated to dryness in a platinum crucible, yet avoiding a red heat, and the sulphate of zirconia may then be dissolved in boiling water.—Ed.

AMMONIA behaves in the same manner.

Solution of CARBONATE OF POTASH determines, in solutions of zirconia, a voluminous precipitate of carbonate of zirconia, soluble in a large excess of the re-agent.

Solution of BICARBONATE OF POTASH behaves in the same manner, * but it dissolves a little more zirconia.

Solution of CARBONATE OF AMMONIA reacts in the same manner; an excess of the re-agent redissolves also the precipitate a little more freely than solution of carbonate of potash.

A solution of PHOSPHATE OF SODA produces a voluminous precipitate of phosphate of zirconia in solutions of zirconia.

A solution of OXALIC ACID gives a bulky precipitate of oxalate of zirconia, which is soluble only in a great excess of muriatic acid.

A concentrated solution of SULPHATE OF POTASH determines, after some time, a white precipitate, which is a double sulphate of potash, and of zirconia, soluble in a large quantity of muriatic acid. When this precipitate is produced in a hot solution it is almost insoluble in water and in acids.

A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate*—produces a white precipitate.

A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash*) does not form any precipitate.

HYDROSULPHURET OF AMMONIA produces a bulky precipitate of hydrate of zirconia. * An extremely feeble quantity of sesquioxyde of iron (peroxyde of iron—*oxyde ferrique*) mixed with the zirconia, is sufficient to render this precipitate of a grey or of a black colour.

SULPHURETTED HYDROGEN, in solution or in the gaseous state, does not form any precipitate.

Neutral solutions of zirconia redden litmus paper.

The salts of zirconia, which are soluble in water, are decomposed by a red heat.

The compounds which zirconia forms with acids, when not soluble in water, are, in some cases, difficult to distinguish from pure zirconia.

It is impossible before the blow-pipe to distinguish in a satisfactory manner zirconia from substances which resemble it. * Heated with the blow-pipe, it gives a very powerful light[1].

Solutions of zirconia are distinguished from those of the alkalies, and likewise from those of baryta, strontia, lime, and magnesia, by the same characters which establish a difference between these and the solutions of alumina. Zirconia is distinguished from alumina and from glucina by its insolubility in an excess of potash; from thorina and yttria, because when a hot solution of sulphate of potash is poured in a solution of zirconia, a precipitate is obtained, almost insoluble in water, and even in acids[2], whilst the precipitates furnished by thorina and yttria are soluble in a great quantity of water. Zirconia differs also from yttria, because, after having been subjected to a red heat, it is insoluble in acids, except in sulphuric acid, whilst yttria, treated in the same manner, is pretty easily soluble in muriatic acid. Lastly, it may be distinguished from protoxyde of cerium, because, when exposed to a red heat, it does not assume the red brick colour as sesquioxyde of cerium does, and because, when treated before the blow-pipe either with borax or salt of phosphorus (microscomic salt), it yields a glass which is colourless, both before and after cooling, provided always that it contains no iron.

The presence of non-volatile organic substances prevents the precipitation of zirconia from such solutions by alkalies[3].

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[1] Berzelius says, that this substance throws before the blow-pipe a more powerful light than any he ever tried; it is so dazzling even by daylight that the eye can hardly bear it.—Ed.

[2] This insoluble combination, according to Berzelius, is a basic salt in which the acid is combined with six times as much base as in the neutral salt, and the quantity of potash is at the same time so small, that it might be looked upon as not being essential to the combination if sulphate of soda did produce an analogous precipitate, which however it does not.—Ed.

[3] Sulphite of ammonia in excess produces the same effect.—Ed.

15. OXYDES OF MANGANESE.

1°. PROTOXYDE OF MANGANESE [MO].

(*Oxyde Manganeux.*)

In analytical researches protoxyde of manganese is seldom met with in a state of purity[1], but when this occurs it is pulverulent, and of a greyish-green colour. By exposure it gradually absorbs oxygen, provided it be not kept at too high a temperature, and becomes brown, a circumstance which does not take place when prepared under the influence of a high heat[2]. When free from deutoxyde of manganese it dissolves in hot muriatic acid without chlorine being disengaged. The hydrate of protoxyde of manganese is white, but it very rapidly absorbs the oxygen of the air, in consequence of which it soon assumes a brown colour. Its salts are white, yet they generally have a feeble red or pink tint. Once in the saline state, and even then when dissolved, protoxyde of manganese is not converted into deutoxyde by the contact of the air.

A solution of POTASH produces in solutions of protoxyde of manganese a white precipitate of hydrate of protoxyde, which by exposure speedily becomes yellowish, then brown, and, lastly, black; all these changes are the result of the absorption of the oxygen of the air, and is more particularly observable at those points which are in contact with the air[3]. If in a solution of protoxyde of manganese a solution of muriate of ammonia be poured, and next after that a solution of potash, a white precipitate is likewise produced, but not so abundantly, and which does not turn brown so rapidly by contact with the air.

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[1] Though protoxyde of manganese is seldom met with *in the pure state*, it is this oxyde which forms the base of nearly all the salts of manganese, for the salts of the peroxyde resolve themselves most easily into salts of protoxyde with disengagement of oxygen.—Ed.

[2] This refers to the two modes of preparing protoxyde of manganese, one of which processes is Professor Faraday's, which consists in first obtaining a protochloride of manganese, by submitting the peroxyde to fusion with sal-ammoniac, lixiviating, evaporating to dryness, and fusing the residuum again with a small quantity of sal-ammoniac and a quantity of pure anhydrous carbonate of soda in a covered crucible. By lixiviating with water, a greyish-green protoxyde is left, which may be washed and dried without further oxydisement; but when protoxyde of manganese is reduced at a low temperature by means of hydrogen gas, it acquires oxygen from the air.—Ed.

[3] This black or brownish-black powder is a hydrate of peroxyde.—Ed.

AMMONIA produces in neutral solutions of proto-salts of manganese a white precipitate of hydrate of protoxyde, which by exposure speedily turns brown, and ultimately black wherever it is in contact with the air[1]. If a solution of muriate of ammonia have first been poured in a solution of protoxyde of manganese, ammonia does not produce any precipitate. A solution of muriate of ammonia readily dissolves the precipitate which ammonia may have determined in solutions of protoxyde of manganese; but such a solution, if left exposed to the air, though clear and limpid at first, gradually becomes brown, and deposits deutoxyde of manganese in the shape of an insoluble brownish-black powder. This phenomenon is first produced at the surface of the liquor, and the oxyde which has there separated adheres to the sides of the vessel. When a precipitate has been produced in a solution of protoxyde by pouring ammonia into it, and if the whole be left exposed for a long time, until in fact the precipitate has become brown, a solution of muriate of ammonia dissolves the protoxyde which may be still left, but does not act upon the brownish-black deutoxyde which has been formed under the influence of the atmosphere.

A solution of CARBONATE OF POTASH determines in solutions of protoxyde of manganese a white precipitate of carbonate of manganese, which does not undergo any change of colour by exposure[2], and which is but sparingly soluble in a solution of muriate of ammonia.

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[1] According to Berzelius, caustic ammonia poured in a neutral solution of protoxyde of manganese precipitates half the oxyde therefrom, and forms with the other half a double salt, in which ammonia and protoxyde of manganese saturate the same quantity of acid. If the solution be acid, ammonia forms a double salt, and no precipitate is produced, however large the excess of ammonia added to the solution may be.—ED.

[2] Berzelius says, that the white precipitates formed by the alkaline carbonates in solutions of salts of protoxyde of manganese, assume after some time an amethyst colour, when left exposed to the air.—ED.

A solution of BICARBONATE OF POTASH produces a white precipitate in solutions of protoxyde of manganese; this precipitate requires some time for its production when the solutions are diluted. If a solution of protoxyde contains any muriate of ammonia, bicarbonate of potash does not create an immediate precipitate, but after some time one appears.

A solution of CARBONATE OF AMMONIA determines in solutions of protoxyde of manganese a white precipitate of carbonate of manganese, which does not change colour by contact with the air, and which is almost insoluble in a solution of muriate of ammonia.

A solution of PHOSPHATE OF SODA produces in solutions of protoxyde of manganese a white precipitate of phosphate of manganese inalterable by exposure.

A solution of OXALIC ACID determines after some time in neutral solutions of protoxyde of manganese a white crystalline precipitate of oxalate of manganese insoluble in free oxalic acid[1]. This crystalline precipitate of oxalate of manganese is formed even when a solution of oxalic acid is poured in a concentrated solution of sulphate of protoxyde of manganese, but the crystals in question are not produced in dilute solutions. These crystals are likewise soluble in sulphuric or in muriatic acid. Solutions of oxalates produce the same crystalline precipitate of oxalate of manganese in dilute solutions of protoxyde of that metal. If a solution of oxalic acid, or of an oxalate, be poured into a dilute solution of protoxyde of manganese, and no precipitate be thereby formed, an addition of ammonia determines its production. Yet if the solution of protoxyde of manganese contain muriate of ammonia, or if it be acid, or, lastly, if a considerable quantity of oxalic acid, or of an oxalate, have been poured into it, the further addition of ammonia does not form any precipitate; but if the liquor be then left exposed, an insoluble brownish-black precipitate of sesquioxyde of manganese subsides.

A solution of FERROCYANURET OF POTASSIUM—*yellow prussiate*

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[1] Oxalate of manganese is sparingly soluble in water, and in drying its white colour assumes a pink hue.—ED.

of potash—produces in solutions of protoxyde of manganese a white precipitate with a reddish [or orange grey] colour, and soluble in free acids[1].

A solution of FERRICYANURET OF POTASSIUM—*red prussiate of potash*—gives a brown precipitate insoluble in free acids.

* INFUSION OF GALLS produces no precipitate in neutral solutions of protoxyde of manganese.

HYDROSULPHURET OF AMMONIA determines in neutral solutions of protoxyde of manganese a precipitate of a flesh colour inclining to yellow, which is sulphuret of manganese. In order to judge well of the colour of the precipitate, when not abundant, it should be examined only after it has entirely subsided at the bottom of the vessel, because its tint does not appear pure whilst it is suspended in the liquor which is tinged yellow by the excess of the re-agent, on account of the great quantity of sulphur which it holds in solution. The precipitate is insoluble in an excess of hydrosulphuret of ammonia. When the flesh-coloured precipitate of sulphuret of manganese is exposed to the air, which occurs, for example, whilst gathering it on the filter, its surface soon becomes oxydised, and in a short time it becomes brownish-black.

* If the salt of protoxyde of manganese contain any trace of iron, the precipitate produced by hydrosulphuret of ammonia will appear grey or even black[2].

SULPHURETTED HYDROGEN in aqueous solution, or in the gaseous state, produces no precipitate of sulphuret of manganese in neutral solutions of protoxyde of manganese, unless the acid which constitutes the salt be a very weak acid; but after the addition of solution of sulphuretted hydrogen, a pale flesh-coloured precipitate of sulphuret of manganese is formed by the further addition of ammonia.

* Aqueous solution of sulphuretted hydrogen gas does not at first produce any precipitate in a solution of neutral acetate of manganese; but after some time a little sulphuret of manganese

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[1] Berzelius says, that the precipitate produced by ferrocyanuret of potassium is white, and gradually becomes pinkish by exposure.—ED.

[2] Owing to the sulphuret of iron then produced, and which is black.—ED.

separates. If, however, free acetic acid be added to the liquor, no precipitation of sulphuret of manganese takes place[1].

Among the salts of protoxyde of manganese which are soluble in water, and which contain no organic acids, the sulphate is the only one which may be exposed to a red heat in contact with the air without undergoing decomposition; but even this salt, if submitted to too strong a heat, is no longer completely soluble in water.

Solutions of salts of protoxyde of manganese have no action upon blue litmus paper.

The combinations of protoxyde of manganese with acids which in the neutral state are not soluble in water, dissolve in free acids; for example, in dilute sulphuric acid or in muriatic acid. The presence of protoxyde of manganese in such solutions can be detected by neutralising the free acid with ammonia, and then adding hydrosulphuret of ammonia, which produces the characteristic yellowish flesh-coloured precipitate of sulphuret of manganese. The salt of protoxyde of manganese, insoluble in water, is ordinarily precipitated by ammonia with its peculiar white colour of hydrate of manganese, which the addition of hydrosulphuret of ammonia converts into a flesh-coloured precipitate. When protoxyde of manganese is combined with an acid precipitable by hydrosulphuret of ammonia in the state of sulphuret, such as, for example, arseniate of manganese [by which a sulphuret of arsenic is formed at the same time], it is necessary to add an excess of hydrosulphuret of ammonia, which dissolves the metallic sulphuret [sulphuret of arsenic] produced, whilst sulphuret of manganese remains undissolved[2].

Salts of protoxyde of manganese are very remarkable and well characterised by their behaviour before the blow-pipe. When exposed to the exterior flame upon charcoal with borax, or microcosmic salt, they dissolve and assume an amethyst colour, which completely disappears in the interior flame, and re-appears in the exterior one[1]. The smallest quantities of a salt of protoxyde of manganese may be detected before the blow-pipe by fusing them with soda on a platinum foil; the melted mass then assumes a green tint[2].

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[1] Berzelius says, that the alkaline *chromates* produce no precipitate in solutions of protosalts of manganese, but that, after a certain time, a brown precipitate falls down, owing to the decomposition of the chromate.—Ed.

[2] Most salts of protoxyde of manganese are soluble in water, and their solutions are colourless or pinkish, and often become turbid or brown by exposure to the air. —Ed.

Solutions of proto-salts of manganese are so well distinguished by their behaviour with hydrosulphuret of ammonia, that it is impossible to confound them with those of the alkalies and of the earths.

* Non-volatile ORGANIC SUBSTANCES, for example, *tartaric acid*, may interfere with the precipitation of protoxyde of manganese from such solutions. When a solution of protoxyde of manganese contains much organic matter, the best way is to precipitate the oxyde by means of hydrosulphuret of ammonia, and to try the sulphuret thus obtained before the blow-pipe. If protoxyde of manganese be contained in organic substances in the solid or in the pasty state, it is sufficient to incinerate a little of the mass upon a piece of platinum foil before the flame of the blow-pipe, and to melt the residuum with soda upon platinum foil.

2° DEUTOXYDE OF MANGANESE, Mn_2O_3.

[SESQUIOXYDE OF MANGANESE.]

(*Oxyde Manganique*).

PURE deutoxyde of manganese (*oxyde manganique*) has a black colour, or when in a state of extreme division it has a brown tint. When its powder is not too fine, it is black. It dissolves in muriatic acid, with which it produces a deep brown liquid, which even in the cold exhales the smell of chlorine, because there is always a portion of deutochloride of manganese undergoing reduction to the state of protochloride. When deutochloride of manganese is boiled with muriatic acid, the formation of protochloride of manganese is rapid: the liquor loses then its deep hue, whilst, at the same time, a strong smell of chlorine is evolved. The boiled solution behaves then with re-agents like a solution of protoxyde. If deutoxyde of manganese be digested with sulphuric acid,somewhat diluted, it dissolves and produces a violet liquor which, being submitted to ebullition, is decomposed and disengages oxygen gas; but the reduction is less rapid than that of the solution in muriatic acid; yet the decomposition is easily effected when the solution is heated, adding, at the same time, non-volatile organic substances thereto, for example, sugar. Deutoxyde of manganese is very sparingly soluble in nitric acid. The solution is, however, rapidly effected with disengagement of carbonic acid gas when sugar or other organic substances are added; the liquid thus obtained is colourless and contains protoxyde of manganese.

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[1] According to Berzelius, when the proportion of protoxyde of manganese is very large, it assumes with borax such a deep amethyst tint in the exterior flame that it appears black; by drawing it into a thread, however, its proper colour may be seen. With salt of phosphorus, the colour is never so deep as to cease being transparent. If the glass produced by the salt of phosphorus contains so feeble a quantity of manganese as not sensibly to colour the glass, the colour may be rendered manifest by the application of a crystal of saltpetre on the liquid bead, which causes the mass to froth up, and the froth on boiling assumes a pale pink or an amethyst colour, according to the quantity of manganese contained therein.—ED.

[2] In this manner $\frac{1}{1000}$ of manganese imparts a sensible green colour to the soda. —ED.

The hydrate of deutoxyde of manganese, which is found in nature, is very much like the peroxyde, and in commerce may often be mistaken for it, because it has a black colour when in crystals like that of the peroxyde, and because it is necessary to reduce it in extremely fine powder to develop the brown colour which characterises that obtained by precipitation. It may, however, be distinguished from the peroxyde, because it gives a brown streak upon unglazed china, whilst peroxyde gives a black streak, and also because it disengages aqueous vapours when heated in a small glass tube, closed at one end.

Before the BLOW-PIPE, deutoxyde of manganese and its combinations behave like protoxyde and proto-salts of manganese.

A solution of POTASH produces a voluminous brown precipitate when poured in the muriatic solution of deutoxyde of manganese. The presence of muriate of ammonia does not hinder the action of this test, nor of the following ones.

AMMONIA behaves in the same manner.

A solution of CARBONATE OF POTASH determines a voluminous brown precipitate of hydrate of deutoxyde of manganese in the muriatic acid solution of deutoxyde of manganese.

A solution of BICARBONATE OF POTASH produces the same effect.

A solution of CARBONATE OF AMMONIA behaves in the same manner.

A solution of PHOSPHATE OF SODA forms a brown precipitate of phosphate of manganese in the muriatic acid solution of the deutoxyde; but this solution must then previously be neutralised as exactly as possible with ammonia. This precipitate has a lighter colour, and is still much more bulky than those obtained by the preceding re-agents.

A solution of OXALIC ACID does not produce any precipitate in the solutions of deutoxyde of manganese. Yet, after a certain time, the liquor becomes colourless.

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash) determines a greyish-green precipitate.

A solution of FERRICYANURET OF POTASSIUM yields a brown precipitate in that solution, as well as in those of protoxyde of manganese.

HYDROSULPHURET OF AMMONIA produces in a solution of deutoxyde of manganese, previously saturated with ammonia, the same flesh-coloured precipitate of sulphuret of manganese as in solutions of protoxyde of manganese. If the solution of deutoxyde of manganese has been saturated with ammonia, and if the deutoxyde has thus been precipitated in the form of a deep brown powder, this precipitate becomes flesh-coloured and is converted into sulphuret of manganese by the addition of hydrosulphuret of ammonia.

SULPHURETTED HYDROGEN, either liquid or gaseous, determines in solutions of deutoxyde of manganese a milky white precipitate of sulphur, whilst the deutoxyde is reduced to protoxyde of manganese.

3° RED OXYDE OF MANGANESE $MnO+Mn_2O_3$.

[MANGANOSO MANGANIC OXYDE.]

(*Oxyde Mangano-manganique*).

* A COMBINATION of protoxyde and of deutoxyde of manganese ($MnO+Mn_2O_3$) is formed when a mixture of carbonate of protoxyde of manganese, and of deutoxyde or of peroxyde of manganese are exposed to a strong red heat in contact with the air[1]. This combination is likewise met with in nature. It has a brown-red colour, and is unalterable in the air. When boiled with concentrated nitric acid, it is converted into protoxyde of manganese, which dissolves in the acid and into deutoxyde of manganese, which remains undissolved.

4°. PEROXYDE OF MANGANESE MnO_2.

(*Suroxyde de Manganèse.*)

PEROXYDE of manganese[2] is black, and its crystals leave a streak of a pure black upon unglazed china. When exposed to a red heat, it becomes brown, and disengages oxygen, becoming converted into manganoso-manganic oxyde; yet a pretty strong heat is required to produce this effect if the calcining takes place out of the contact of the air. Pure peroxyde of manganese does not yield any water when heated in a glass tube closed at one end,—if when so heated, any aqueous vapours are seen, it is a proof that it contains hydrate of deutoxyde, which is of frequent occurrence. Peroxyde of manganese is soluble in muriatic acid with disengagement of chlorine gas, and gives a brown liquor which contains perchloride of manganese. * This conversion takes place more rapidly when certain organic substances are added, especially such as are not volatile, as for example, sugar; yet, if too much of this last substance be employed, the solution assumes a brown colour. Peroxyde of manganese dissolves in sulphuric acid, but heat must be applied; oxygen gas is disengaged, and a violet liquor is produced, which contains deutoxyde of manganese. It is very slightly soluble in dilute sulphuric acid, and also in nitric acid, even though a boiling heat be applied. The addition of sugar, or of other organic substances, greatly promotes the solution, which is then effected with disengagement of carbonic acid gas; but the re-action of the sulphuric acid upon the organic matter often causes the liquor to become black; this liquor contains protoxyde of manganese. Organic acids, such as for example tartaric acid, dissolve peroxyde of manganese, and carbonic acid is disengaged; the solution likewise contains protoxyde of manganese. The presence of organic substances promotes the solution; but the peroxyde is then converted into protoxyde of manganese and carbonic acid is disengaged, but neither chlorine nor oxygen gas are evolved.

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[1] Berzelius says, that this manganoso-manganic oxyde is always formed whenever any of the oxydes of manganese are strongly heated. The natural production is called Hausmannite by mineralogists.—ED.

[2] In commerce, it is known under the name of *manganese*. Mineralogists call it pyrolusite (from πυρ, fire, and λουω, I wash), because it has the property of discharging the brown and green tints of glass which are caused by peroxyde of iron.—ED.

16. OXYDE OF ZINC ZnO.

[OXYDE ZINCIQUE].

Pure protoxyde of zinc is white, when heated it becomes of a yellow lemon colour, but again becomes white on cooling. * Sometimes, however, pure oxyde of zinc retains after cooling a pale yellow tinge, especially when it has been very strongly heated; in many cases, on the contrary, this yellow colour is derived from some peroxyde of iron, with which it is mixed[1].

It is not volatilisable by heat, and readily dissolves in acids, even after having been strongly heated. Its salts are absolutely colourless[2].

A solution of potash produces, in solutions of protoxyde of zinc, a white gelatinous precipitate of hydrate of protoxyde of zinc, which is re-dissolved by an excess of the re-agent.

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[1] According to Berzelius, crystallised oxyde of zinc is always yellow, transparent, and opaque: the crystals are short six-sided prisms.—Ed.

[2] Except the double chromate of zinc and of potash, which has a fine orange-yellow colour, and chromate of zinc, which is purple brown.—Ed.

AMMONIA behaves in the same manner.

A solution of CARBONATE OF POTASH determines in solutions of oxyde of zinc a white precipitate of subcarbonate of zinc, which is altogether insoluble in any excess of the re-agent, but which, on the contrary, is readily dissolved by solution of potash, or of ammonia. If the solution contains much muriate of ammonia, solution of carbonate of potash does not produce any precipitate in the cold; but after prolonged boiling a precipitate appears, because the ammoniacal salt is easily decomposed by boiling (in contact with an alkali, or an alkaline carbonate[1]).

A solution of BICARBONATE OF POTASH produces a white precipitate, and carbonic acid is disengaged.

A solution of CARBONATE OF AMMONIA produces a white precipitate, soluble in an excess of the re-agent.

A solution of PHOSPHATE OF SODA produces in neutral solutions of protoxyde of zinc, a white precipitate of phosphate of zinc, soluble in acids as well as in potash and ammonia.

A solution of OXALIC ACID produces in neutral solutions of protoxyde of zinc, a white precipitate of oxalate of zinc, which augments by standing. It is true that this re-agent does not produce an immediate precipitate in very dilute solutions, but after a certain time such solutions become turbid. A solution of binoxalate of potash likewise produces a precipitate.

The precipitate produced by oxalic acid in solutions of protoxyde of zinc is soluble in potash and in ammonia, and also in muriatic and other acids. The presence of muriate of ammonia does not hinder much its production.

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash) produces in solutions of protoxyde of zinc, a white gelatinous precipitate, insoluble in free muriatic acid.

* If the solution be acid, the precipitate assumes a blueish tinge, which is owing to the decomposition of the excess of the re-agent; frequently also it assumes a strong blue colour when heated.

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[1] This precipitate is always produced by the addition of an alkaline carbonate, even in the cold; it is a combination of 3 at. of hydrate of protoxyde of zinc, with 2 at. of carbonate of zinc, $3\ (ZnO + HO) + 2\ (ZnO, Co_2.)$—ED.

A solution of FERRICYANURET OF POTASSIUM determines in solutions of protoxyde of zinc, an orange-yellow precipitate, which is soluble in free muriatic acid.

* INFUSION OF GALLS does not determine any precipitate in neutral solutions of protoxyde of zinc.

If the solution contains traces of peroxyde of iron, the fusion of gall-nuts imparts a blue-black tinge. If it contains traces of protoxyde of iron, as is often the case when operating upon crystallised salts of zinc, the infusion of gall-nuts does not at first produce any precipitate; but after a short time's exposure to the air a turbidness of a blue-black colour is formed.

HYDROSULPHURET OF AMMONIA creates in neutral solutions of protoxyde of zinc, a white precipitate of sulphuret of zinc, which is insoluble in an excess of the re-agent, and also in solutions of pure alkalies and of alkaline carbonates[1]. If the solution contain the least trace of proto or of peroxyde of iron, the colour of the precipitate is grey, and if the proportion of iron be more considerable, the precipitate is black.

SULPHURETTED HYDROGEN GAS produces a white precipitate in neutral solutions of protoxyde of zinc; but this re-agent does not produce any precipitate in acid solutions of protoxyde of zinc, especially when the acid is not a weak one[2].

* Sulphuretted hydrogen dissolved in water precipitates protoxyde of zinc completely in the state of sulphuret of zinc, not only from a neutral solution, but likewise from one to which a large quantity of acetic acid has been added. If, on the contrary, the solution contains only a small quantity of a strong inorganic acid, the separation of the oxyde of zinc is not complete.

All the salts of oxyde of zinc which are soluble in water, are decomposed when exposed to a red heat in contact with the air, and they are then no longer soluble in water. Sulphate of zinc, however, when so heated, is only partially decomposed, even though it be submitted to a very strong red heat.

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[1] This precipitate of sulphuret of zinc is readily soluble in muriatic and in dilute sulphuric acid, insoluble in acetic acid. It is a bulky precipitate difficult to filter; by standing, however, the supernatant liquor may easily be decanted.—ED.

[2] It is necessary that the solution should be *acid*, and to take care that it should not merely have an acid reaction, which would be the case with a *neutral* solution, since all neutral solutions of zinc-salts redden litmus paper, and from such a neutral solution a white precipitate of sulphuret of zinc is thrown down, even though the acid in solution be a strong one, for example, sulphuric acid.—ED.

* When protoxyde of zinc, or a zinc-salt, is calcined with an excess of carbonate of potash or of soda, the water with which the fused mass may be subsequently treated, does not dissolve the least trace of oxyde of zinc.

Neutral solutions of zinc-salts redden litmus paper.

The zinc-salts, which are insoluble in water, are soluble in free acids; for example, in dilute sulphuric or muriatic acids. When the acid solution is saturated with ammonia or with potash, the insoluble zinc-salt is precipitated, it is true, but it is ordinarily redissolved by an excess of the re-agent. Hydrosulphuret of ammonia, poured in such an alkaline solution, precipitates the whole of the oxyde of zinc in the state of white sulphuret of zinc. This is, in fact, the best way of ascertaining the presence of oxyde of zinc in the zinc-salts, which are insoluble in water, for the white precipitate which hydrosulphuret of ammonia determines in a clear, strongly alkaline, solution can be nothing else than sulphuret of zinc[1].

That which particularly identifies zinc-salts before the *blow-pipe* is, that when mixed with soda, and heated upon charcoal in the interior flame, the charcoal becomes covered with a white fur of protoxyde of zinc[2]. When moistened with solution of proto-nitrate of cobalt, and then heated before the blow-pipe, the fused mass will have a beautiful green colour.

Zinc-salts solutions may be distinguished from those of the alkaline salts by their behaviour with carbonate of potash, and from those of the earthy salts, because those of zinc, after having been dissolved by potash or ammonia, give a white precipitate when treated by hydrosulphuret of ammonia, a phenomenon which does not take place even in solutions of alumina in potash.

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[1] If, however, the solution under examination should contain much ammoniacal salt, protoxyde of manganese might at the same time exist in such a solution as well as zinc, and the precipitate produced by hydrosulphuret of ammonia might eventually be a sulphuret of both metals. M. Otto (*Annalen der Chemie und Pharmacie*, xlii.), has proposed the following method to separate zinc from manganese when they exist in solutions which contain a large proportion of muriate of ammonia. Ammonia is added, which does not produce any precipitate, but the two metals may then be precipitated by a current of sulphuretted hydrogen. The sulphuret of manganese (if any be present), may be dissolved by acetic acid, in which sulphuret of zinc is insoluble.—Ed.

[2] This white fur appears yellow whilst hot, and becomes white in cooling.—Ed.

When a solution of protoxyde of zinc contains much non-volatile organic matter, the way to detect the presence of oxyde of zinc therein, consists in saturating it with ammonia, and filtering it, if a precipitate is thereby produced. Hydrosulphuret of ammonia is then to be poured in the filtered solution, which precipitates the oxyde of zinc in the state of sulphuret of zinc, which is subsequently to be heated by the blow-pipe, especially when the precipitate instead of being white is grey or black from some sulphuret of iron which may have been precipitated at the same time. It is often very difficult to detect a small quantity of oxyde of zinc in solid or pasty animal substances. It is then necessary to digest these substances in dilute nitric acid, to filter the liquid, and then to treat it, as we have just said, with ammonia and hydrosulphuret of ammonia. One may also begin by carbonising the organic substance, but to effect this a moderate heat only should be applied, for otherwise the oxyde might be reduced to the metallic state, which would then volatilise: the mass being carbonised, it is to be digested in nitric acid, and the solution may then be treated in the manner which has been indicated.

The presence of non-volatile organic substances opposes less resistance to the precipitation of oxyde of zinc by alkalies than any other metallic oxyde.

17. OXYDES OF COBALT.

1° PROTOXYDE OF COBALT CoO.

(*Oxyde Cobaltique.*)

PURE protoxyde of cobalt is of a greenish-grey colour, but its dry hydrate is reddish. It dissolves in acids, as it is often mixed with some peroxyde of cobalt; an odour of chlorine is frequently emitted whilst dissolving in muriatic acid.

* Salts of cobalt are red when they contain water of crystallisation, in the anhydrous state they are blue. Their solutions

are red, yet when concentrated or when they contain a free acid they are blue or green, but they become green simply by the addition of water.

A solution of POTASH produces in cobalt solutions a blue precipitate of protoxyde of cobalt, which becomes green by exposure to the air, part of the protoxyde becoming thus converted into peroxyde. By boiling, the blue precipitate of protoxyde of cobalt acquires ordinarily, but not always, a dirty pale-red colour without undergoing on that account any notable change in its composition[1]. This pale-red precipitate does not sensibly change by exposure to the air. If the blue precipitate be abandoned at the bottom of the liquid in which it has been produced, it often occurs that after a certain time it acquires a pale-red colour even in the cold. When gathered on the filter this blue precipitate very soon turns green. It is insoluble in an excess of a solution of potash.

* According to Winkelblech, the blue precipitates which protoxyde of cobalt produces with the alkalies are always basic salts. The green colour is owing to the absorption of atmospheric air, which gives rise to the production of some peroxyde of cobalt.

A little AMMONIA causes in solutions of protoxyde of cobalt a blue precipitate, which the addition of a larger quantity of ammonia renders green, and which is redissolved by a still larger addition of ammonia, producing at the same time a brownish-red liquor. The colour of this solution by exposure to the air becomes deeper and deeper, beginning at the surface, and ultimately the whole liquor assumes a brown-red colour[2]. If the solution of protoxyde of cobalt contains muriate of ammonia, the addition of ammonia thereto does not produce any precipitate, but retains its brown-red colour; after some time, however, it becomes of a dark-brown colour, and this change likewise begins at the surface. A solution of potash determines a very slight precipitate only in an ammoniacal solution of protoxyde of cobalt, and if the liquor contains a little muriate of ammonia, no precipitate at all is produced by this re-agent.

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[1] According to Proust, this dirty red precipitate is a hydrate of protoxyde.—ED.

[2] According to Berzelius, the solution of protoxyde of cobalt in ammonia and in carbonate of ammonia, has a fine red colour if the protoxyde of cobalt is pure; but if the said protoxyde of cobalt contains more or less nickel, the hue of the solution may become dirty purple, or even brownish black. Caustic potash does not precipitate protoxyde of cobalt from such a solution.—ED.

A solution of CARBONATE OF POTASH produces in solutions of protoxyde of cobalt, a red precipitate of sub-carbonate of cobalt, which by boiling the liquid becomes blue[1].

A solution of BI-CARBONATE OF POTASH determines a red precipitate of carbonate of cobalt.

A solution of CARBONATE OF AMMONIA gives in neutral solutions of protoxyde of cobalt a red precipitate of carbonate of cobalt, which is soluble in a solution of muriate of ammonia. The solution has a red colour, and does not turn brown by exposure, but after a pretty long time it assumes a somewhat deeper hue only, which begins from the surface. When a solution of protoxyde of cobalt contains muriate of ammonia, carbonate of ammonia produces no precipitate therein.

A solution of PHOSPHATE OF SODA yields a blue precipitate of phosphate of cobalt in neutral solutions of protoxyde of cobalt.

A solution of OXALIC ACID does not cause any immediate turbidness in solutions of protoxyde of cobalt; but after some time a white precipitate of oxalate of cobalt is formed, which has, however, a slight reddish tint. This precipitate gradually augments, so that after some time the supernatant liquor is almost colourless[2].

A solution of FERROCYANURET OF POTASSIUM determines in solutions of protoxyde of cobalt a green precipitate of ferrocyanuret of cobalt, which afterwards becomes grey, and which is insoluble in muriatic acid.

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[1] According to Dumas, the precipitate produced in solutions of sulphate of cobalt by carbonate of potash, is a sesquicarbonate of cobalt, which has a pink colour; but if an excess of carbonate of ammonia has been used, much of that precipitate is re-dissolved, because carbonic acid is set free, and forms a bicarbonate in which this precipitate is soluble, though boiling throws it down in the state of carbonate of cobalt. If an excess of bicarbonate of potash is added whilst the above precipitate is forming, a double salt is obtained, which boiling reduces to the state of carbonate of cobalt.—ED.

[2] This precipitate is sparingly soluble in caustic ammonia, but more so in carbonate of ammonia.—ED.

A solution of FERRICYANURET OF POTASSIUM produces in solutions of protoxyde of cobalt a deep brown-red precipitate of ferricyanuret of cobalt, which is insoluble in muriatic acid.

* INFUSION OF GALL-NUTS does not render solutions of protoxyde of cobalt turbid.

HYDROSULPHURET OF AMMONIA causes in neutral solutions of cobalt a black precipitate of sulphuret of cobalt, which is insoluble in an excess of the re-agent, and which completely falls down at the bottom of the vessel. * This precipitate is not soluble in solutions of the pure alkalies, nor of alkaline carbonates.

A solution of SULPHURETTED HYDROGEN does not immediately cause any precipitate in neutral solutions of protoxyde of cobalt, at least when the acid of the salt is not an extremely weak acid. The liquor acquires only a somewhat blackish hue, and after some time a very scanty black precipitate of sulphuret of cobalt is deposited.

* If the solution of protoxyde of cobalt be acid, not the slightest black turbidness takes place, even after a long time. Aqueous solution of sulphuretted hydrogen completely precipitates the protoxyde of cobalt in the state of sulphuret, from a neutral solution of acetate of cobalt. If on the contrary free acetic acid be added to the neutral solution, nothing is precipitated, and the whole of the protoxyde remains dissolved after the addition of sulphuretted hydrogen[1].

All the salts of oxyde of cobalt which are soluble in water, are decomposed by exposure to a red heat with the contact of the air, after which they are no longer completely soluble in water. A very strong red heat, however, only partially decomposes sulphate of cobalt[2].

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[1] Brande observes, that if chlorine be passed through a mixture of protoxyde of cobalt and water, or when a solution of chloride of cobalt is decomposed by chloride of lime, a black precipitate falls, which is hydrate of peroxyde of cobalt.—ED.

[2] After a protracted ignition, it is converted into an oxyde, which is blackish blue. If only heated to 500°, the crystals of sulphate of cobalt fall into a blue

Solutions of neutral salts of cobalt feebly redden blue litmus paper.

Almost all the salts of oxyde of cobalt which are insoluble in water, are soluble in acids, such as for example, in muriatic and in sulphuric acids. If such a solution be saturated with potash, or, still better, with ammonia, the insoluble compound is precipitated, but it is ordinarily re-dissolved by an excess of ammonia. If the solution be very acid, no precipitate is produced by supersaturating it with ammonia, because the ammoniacal salt produced hinders precipitation from taking place; but then hydrosulphuret of ammonia determines an immediate black precipitate of sulphuret of cobalt, and this is the character most to be depended upon to detect protoxyde of cobalt in a solution; for when sulphuretted hydrogen gas does not produce any precipitate in an acid solution, whilst hydrosulphuret of ammonia produces a black precipitate in neutral or in an alkaline solution, such a precipitate can hardly be anything else than sulphuret of cobalt, or of nickel, or of iron. It will be shown further on, how these sulphurets can be distinguished from each other.

Before the *blow-pipe* salts of cobalt are very easy of detection, the smallest quantity being sufficient to impart a strong blue colour to borax and to microcosmic salt, both in the exterior and the interior flame. When the quantity of the salt of cobalt is abundant, the colour of the glass is so intensely blue that it appears black. With soda (on charcoal) these salts are reduced into a magnetic grey powder, which is metallic cobalt[1].

Solutions of salts of cobalt are distinguished from those of all the other salts which have been hitherto treated of, principally by the black precipitate of sulphuret of cobalt, which hydrosulphuret of ammonia produces therein; in the solid

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powder, and which is anhydrous sulphate of cobalt, forming a pink solution with water, whilst it becomes of a lavender colour by exposure. Sulphate of cobalt is insoluble in alcohol, soluble in 24 parts of cold water.—Ed.

[1] Berzelius remarks, that by candlelight, the colour of the glass obtained with microcosmic salt is purple, whilst by daylight it is of a pure blue colour; and if by daylight it is tinged feebly blue, by candlelight it appears pink or rose-coloured.—Ed.

state, by the deportment of the salts before the blow-pipe, which is most characteristic and delicate.

A great many non-volatile substances prevent the precipitation of protoxyde of cobalt by alkalies, but they do not interfere with the reaction of hydrosulphuret of ammonia.

2° PEROXYDE OF COBALT Co_2O_3.

[SESQUIOXYDE OF COBALT.]

(*Suroxyde de Cobalt*).

Peroxyde of cobalt is black, but when finely pulverised it is brown. Before the blow-pipe, its deportment is the same as that of the protoxyde.

* When strongly heated, oxygen is disengaged [and it is then reduced to the state of protoxyde.—Ed.] Concentrated muriatic acid dissolves it at a boiling heat, and chlorine is disengaged; but that acid may combine with it at the ordinary temperature[1].

* Acetic acid slowly but completely dissolves its hydrate, and produces a liquor of a deep brown colour, which when much diluted appears yellow. This solution is less decomposed than that of the peroxyde in other acids; solutions of pure fixed alkalies and of alkaline carbonates produce therein a brown precipitate, and the same effect is produced by carbonate of ammonia. Ammonia also precipitates it, but incompletely[2].

18. OXYDES OF NICKEL.

1° PROTOXYDE OF NICKEL NiO.

(*Oxyde Niccolique*).

In the pure state, protoxyde of nickel is of a deep grey colour; its hydrate is green. It is soluble in acids, and the solution is green. Salts of nickel are green when they contain water of crystallisation, and ordinarily yellow when they are anhydrous.

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[1] According to Berzelius, no other acid except muriatic acid can dissolve sesquioxyde of cobalt. And by solution in that acid, it is transformed into a protochloride of cobalt.—Ed.

[2] Berzelius says, that by digesting peroxyde of cobalt in ammonia, it is dissolved, part of the ammonia undergoing decomposition, and nitrogen being disengaged.—Ed.

A solution of POTASH creates in solutions of salts of nickel an apple-green precipitate of hydrate of protoxyde of nickel, which is insoluble in an excess of alkali, and which is unalterable in contact with the air[1].

A very small quantity of AMMONIA poured in solutions of protoxyde of nickel produces an inconsiderable green turbidness, which disappears rapidly by the addition of a larger quantity of ammonia: the solution has a fine blue colour, with a slight admixture of violet. A solution of potash produces an apple-green precipitate of hydrate of protoxyde of nickel in this ammoniacal solution[2].

A solution of CARBONATE OF POTASH determines in solutions of protoxyde of nickel an apple-green precipitate of subcarbonate of nickel, which has a paler tint than that produced by potash.

A solution of BICARBONATE OF POTASH produces also a light apple-green precipitate of carbonate of nickel, whilst a little carbonic acid is at the same time disengaged.

A solution of CARBONATE OF AMMONIA gives in neutral [not in acid] solutions of protoxyde of nickel an apple-green precipitate of carbonate of nickel, soluble in an excess of the re-agent, and thus producing a greenish-blue liquid.

A solution of PHOSPHATE OF SODA produces in neutral solutions of protoxyde of nickel a white precipitate of phosphate of nickel, which has a green tinge.

A solution of OXALIC ACID does not determine any immediate precipitate in neutral solutions of protoxyde of nickel; but after some time, a greenish precipitate of *oxalate of nickel* is formed, which augments much by standing, so that the supernatant liquid becomes almost colourless[3].

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash) produces in solutions of protoxyde of nickel a white precipitate of ferrocyanuret of nickel, which has a green tinge, and is insoluble in muriatic acid.

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[1] This precipitate is soluble in carbonate of ammonia, and the liquid which results is greenish blue. Potash may reprecipitate it in the state of hydrate of protoxyde of nickel, which is yellow-green. All the salts of ammonia form double salts with oxyde of nickel.—ED.

[2] If the solution of protoxyde of nickel contains a free acid or an ammoniacal salt, ammonia does not produce any precipitate.—ED.

[3] Oxalic acid forms this precipitate of oxalate of nickel in all neutral solutions of nickel.—ED.

A solution of FERRICYANURET OF POTASSIUM (red prussiate of potash) gives in solutions of protoxyde of nickel a greenish yellow precipitate of ferricyanuret of nickel, which is insoluble in muriatic acid.

* Infusion of GALL-NUTS does not create any turbidness in solutions of salts of protoxyde of nickel.

HYDROSULPHURET OF AMMONIA determines a black precipitate of sulphuret of nickel in neutral solutions of protoxyde, and the supernatant liquor retains a black colour. This precipitate is not entirely insoluble in an excess of the re-agent, * nor in the alkalies, owing to which the portion of the precipitated sulphuret thus retained in solution gives the supernatant liquor the black colour just alluded to[1].

SULPHURETTED HYDROGEN dissolved in water, or a current of that gas, does not produce an immediate precipitate in neutral solutions of nickel, at least when the acid of the salt is not a weak one. The liquid becomes slightly tinged with black, and after some time a very small black precipitate of sulphuret of nickel is thrown down. When the solution is acid no turbidness appears even after a long time. * The solution of protoxyde of nickel in acetic acid behaves with aqueous sulphuretted hydrogen like that of protoxyde of cobalt in the same acid[2].

All the salts of nickel, which are soluble in water, are decomposed by exposure to a red heat, after which they are no longer soluble in water. Sulphate of nickel is more difficult to decompose by a strong heat than the other salts of nickel.

Solutions of neutral salts of protoxyde of nickel feebly redden blue litmus paper.

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[1] According to Dr. Fresenius, this sulphuret is readily soluble in nitromuriatic acid, but difficultly so in muriatic acid.—ED.

[2] In acid solutions, sulphuretted hydrogen forms no precipitate whatever, that is, if there be a strong acid free. According to Gay Lussac, the sulphuret of nickel produced from the decomposition of acetate of nickel by sulphuretted hydrogen, is of a deep brown yellow colour, almost black.—ED.

Almost all the salts of nickel, which are insoluble in water, are soluble in acids, for example, in muriatic acid or in dilute sulphuric acid. When their acid solution is supersaturated with ammonia, the salt is not precipitated, because it is held in solution by the excess of alkali; this solution, if not too dilute, assumes a blue colour which immediately shows the presence of protoxyde of nickel.

Before the blow-pipe salts of oxyde of nickel may be recognised, because when heated with borax and microcosmic salt in the exterior flame, the bead assumes a reddish colour, the intensity of which diminishes in cooling, until at last it often entirely disappears.

* With glass of borax, but not with microcosmic glass, the oxyde is reduced in the interior flame, and the glass appears grey, owing to the interposition of a fine powder of metallic nickel, which pervades the mass. If the oxyde of nickel contain oxyde of cobalt, the presence of the latter may be recognised by the blue colour of the bead[1]. Heated with soda upon charcoal, salts of oxyde of nickel are reduced into a white metallic powder, which is magnetic.

Solutions of salts of oxyde of nickel are distinguished from those of the salts which have hitherto been spoken of, except those of cobalt, by their re-action with hydrosulphuret of ammonia. They are distinguished from cobalt solutions by their re-action with ammonia, and by the behaviour of their ammoniacal solutions with potash[2].

A vast number of non-volatile *organic substances*, especially tartaric acid, prevent protoxyde of nickel from being precipitated by alkalies, but not by hydrosulphuret of ammonia.

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[1] See the note, page 5.

[2] If the ammoniacal solution of protoxyde of cobalt contains a salt of ammonia, caustic potash does not produce any precipitate, whilst the like solution of protoxyde of nickel when treated by potash yields an apple-green precipitate of hydrate of nickel.—Ed.

2°. PEROXYDE OF NICKEL, Ni_2O_3.

[SESQUIOXYDE OF NICKEL.]

(*Suroxyde de Nickel.*)

Peroxyde of nickel is black, and disengages oxygen when submitted to a red heat, which converts it into protoxyde of nickel. Concentrated muriatic acid dissolves it, with disengagement of chlorine gas; other acids dissolve it also, but with disengagement of oxygen. Before the blow-pipe its behaviour is the same as protoxyde of nickel[1].

19. OXYDES OF IRON.

1° PROTOXYDE OF IRON, FeO.

(*Oxyde ferreux.*)

Pure protoxyde of iron (*ferrous oxyde*) is almost unknown; neither has its hydrate ever yet been obtained perfectly pure in the dry state, on account of the facility with which it absorbs the oxygen of the air, especially at the surface. When recently prepared it is white. Protoxyde of iron is not only contained in solutions of protosalts of iron, but it is also produced when iron is dissolved in dilute sulphuric acid or in other acids; hydrogen is disengaged whilst the solution is going on.

* Protosalts of iron have a greenish, or blueish-green colour when they contain water of crystallisation. Even in the solid state they have a tendency to become more oxydised, and to be covered with a yellow brown powder of persalt of iron. They are less exposed to this change when they are precipitated by crystallisation from an acid solution. Solutions of protosalts of iron are much more easily oxydised by the influence of the air, and when they are neutral the liquid deposits a yellow-brown powder, which is a basic salt of peroxyde of iron, notwithstanding which the solution, besides protoxyde of iron, contains a more or less considerable quantity of peroxyde of iron.

A solution of **potash** produces in solutions of protoxyde of iron a flocculent precipitate of hydrate of protoxyde, which at first is almost white, but which soon becomes grey on account of the oxygen it absorbs, and which subsequently turns green. This precipitate then takes a deeper tinge, and ultimately it becomes brown-red, where it is in contact with the atmosphere. When the green precipitate is filtered it soon becomes reddish-brown on the filter, because it then offers very numerous points of contact with the air.

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[1] Peroxyde of nickel is soluble in ammonia, with disengagement of nitrogen, and the solution is one of protoxyde. There are no salts of peroxyde of nickel.—Ed.

AMMONIA produces the same phenomena as potash in solutions of protosalts of iron. When solution of muriate of ammonia has been poured in a ferrous solution, the ammonia which is subsequently added does not produce any precipitate; but if the liquor remains exposed to the air, a slight green precipitate of hydrated protoxyde of iron very soon appears, which becomes reddish-brown at the surface.

A solution of CARBONATE OF POTASH produces a precipitate in solutions of protoxyde of iron, which is not attended with any effervescence of carbonic acid. After some time this precipitate of proto-carbonate of iron turns green, and its surface assumes the same reddish-brown colour produced when solution of pure potash is poured in solutions of protoxyde of iron. A solution of muriate of ammonia re-dissolves it, but when the liquor is left exposed to the air, a green precipitate is formed, which becomes reddish-brown at the surface of the liquid. Yet the formation of this precipitate requires a longer time than when ammonia, instead of carbonate of potash, is the re-agent poured in the liquor.

A solution of BICARBONATE OF POTASH produces, in solutions of protoxyde of iron, a white precipitate of protocarbonate of iron, the formation of which is attended with a disengagement of carbonic acid gas.

A solution of CARBONATE OF AMMONIA behaves with solutions of protoxyde of iron like carbonate of potash.

A solution of PHOSPHATE OF SODA produces, in neutral solutions of protoxyde of iron, a white precipitate of protophosphate of iron, which left for a certain time in contact with the air becomes green.

Solutions of OXALIC ACID, and of BINOXALATE OF POTASH, immediately produce a yellow colour in solutions of protoxyde of iron, and after some time a yellow precipitate of protoxalate of iron soluble in an excess of muriatic acid. Neutral alkaline oxalates produce this precipitate immediately, and still more distinctly.

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate) produces in solutions of protoxyde of iron a precipitate, which at the time of its formation would be white, were the experiment to be made altogether out of the contact of the air, but which otherwise has always a light blue colour. This precipitate becomes dark blue by a long exposure. It is not soluble in muriatic acid[1].

A solution of FERRICYANURET OF POTASSIUM (red prussiate) determines in solutions of protoxyde of iron an immediate dark blue precipitate of ferricyanuret of iron (Prussian blue) which is insoluble in acids.

* INFUSION OF GALL-NUTS does not produce any precipitate in neutral solutions of protoxyde of iron, which do not contain any peroxyde of iron; but if they contain any portion of this latter oxyde, as is almost always the case, a blue-black turbidness is produced, which augments, if the liquor is left at rest, and in contact with the air[2].

* A solution of PERCHLORIDE OF GOLD poured in a solution of protoxyde of iron gives a dark brown precipitate, which is metallic gold[3].

* A solution of NITRATE OF SILVER determines in neutral solutions of protoxyde of iron a greyish white precipitate of metallic

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[1] This precipitate is decomposed by free alkalies, and peroxyde of iron is deposited; hence the liquor to be tested by both yellow and red prussiates should be acid; and if the liquor contains the least quantity of peroxyde of iron, the precipitate produced by ferrocyanuret of potassium is at once dark-blue, as also by the addition of nitric acid or of chlorine.—ED.

[2] The addition of a few drops of ammonia added subsequently to the infusion of galls, renders the solution of protosalts of iron of a purple colour.—ED.

[3] The double chloride of sodium and gold, is, according to Ficinus, a very sensitive test for protosalts of iron. By adding a very small quantity of solution of carbonate of soda, a purple precipitate is formed when a few drops of perchloride of gold are further added.—ED.

silver. If a small quantity of a dilute acid, for example sulphuric acid, be added, the precipitate is white. When the solution of protoxyde of iron is in excess, it becomes black, on account of the nitric acid which is set free.

* If NITRIC ACID (somewhat dilute) be poured upon a protosalt of iron, and the whole heated, the liquor which is immediately round the salt becomes of a dark brownish black colour, which colour gradually pervades the whole liquid as the salt becomes dissolved. The same colour may be observed when either a concentrated or a dilute solution of a protosalt of iron is treated by nitric acid. The nitric acid converts a portion of the protoxyde of iron into peroxyde of iron, and the nitric acid becomes converted into nitric oxyde, which dissolves in the solution of the salt of iron which has not yet passed to a superior degree of oxydation, and gives to the liquid a dark brownish black colour. An excess of nitric acid soon causes the colour to disappear; by free exposure to the air the colour vanishes also, and there is a disengagement of ruddy vapours of nitrous acid. If the protosalt of iron be in excess the colour disappears also, owing to the absorption of the oxygen of the air, but for this some time must elapse.

HYDROSULPHURET OF AMMONIA forms in neutral solutions of protoxyde of iron a black precipitate of sulphuret of iron, which by exposure to the air absorbs oxygen, and becomes reddish brown. This character distinguishes sulphuret of iron from sulphuret of cobalt, and from sulphuret of nickel, which do not become oxydised so easily by exposure. Sulphuret of iron is insoluble in an excess of hydrosulphuret of ammonia; *it remains suspended for a long time in the liquid, especially when the operation is carried on upon small quantities of protosalts of iron, and communicates a green [dingy green] colour to the liquor.

Aqueous solution of SULPHURETTED HYDROGEN, or a current of that gas, does not create any precipitate in neutral solutions of protosalts of iron when the acid is not a weak one.

* When a solution of protoxyde of iron becomes milky by the addition of sulphuretted hydrogen, it is owing to a deposition

of sulphur, which shows that the protosalt of iron was mixed with, or contained some persalt of iron.

The protosalts of iron, which are soluble in water, are decomposed by the action of a red heat in contact with the air.

Solutions of neutral protosalts of iron redden litmus paper.

* According to Bonnsdorf, pure protosulphate of iron does not alter the colour of litmus paper; and when it is reddened, it is a proof of the presence of a persalt of iron.

Almost all the protosalts of iron, which are insoluble in water, are soluble in muriatic acid, or in dilute sulphuric acid. When such a solution is supersaturated by ammonia, the insoluble salt is generally precipitated therefrom; but it immediately assumes a black colour, and is converted into sulphuret of iron by the addition of hydrosulphuret of ammonia.

Before the *blow-pipe* protosalts of iron are very easily recognised. For when heated at the external flame upon charcoal with borax, or microcosmic salt, they communicate to the glass a dark red colour, which becomes lighter on cooling; heated in the interior flame, the glass becomes green; but in cooling this colour entirely vanishes, provided the quantity of iron is not considerable. The smallest traces of protosalt of iron impart to microcosmic salt, when dissolved therein, even by the exterior flame, a green colour, which on cooling is less intense, and which when quite cold entirely disappears. Protosalts of iron heated with soda upon charcoal are reduced. After levigation there remains a metallic powder which is magnetic.

Solutions of salts of protoxyde of iron are easily recognised by their behaviour with *hydrosulphuret of ammonia*, and solution of *ferricyanuret of potassium*.

The presence of a great quantity of non-volatile organic substances often completely prevents protoxyde of iron from being precipitated by alkalies.

* If a sufficient quantity of tartaric acid be added to a solution of protoxyde of iron, ammonia does not produce any precipitate in the liquor; but such a liquor assumes a green colour, which after some time, by exposure to the air, becomes yellow, because it becomes oxydised, and the liquor then contains peroxyde of iron.

2° PEROXYDE OF IRON, Fe_2O_3.

[SESQUIOXYDE OF IRON.]

(Oxyde ferrique.)

In the pure state peroxyde of iron has a reddish brown colour when pulverized. Crystallised peroxyde of iron, as it is found in nature, (oligisto-magnetic iron) is grey, and has a metallic lustre[1]. The peroxyde of iron precipitated from its solutions is very bulky, but undergoes an extraordinary contraction by drying; after ignition it is black, yet when pulverized it forms a red powder, as well as the crystallized natural peroxyde—oligist iron. Recently precipitated peroxyde of iron is very soluble in acids, but after ignition it is of much more difficult solution; yet dissolves completely, and in muriatic acid better than in any other acid. * Neutral persalts of iron appear to be white; the basic ones are yellow, brown, or reddish brown.

A solution of POTASH produces in solutions of peroxyde of iron a bulky reddish brown precipitate of hydrated peroxyde, which is insoluble in an excess of potash.

AMMONIA behaves like potash with solutions of peroxyde of iron.

A solution of CARBONATE OF POTASH produces likewise in solutions of peroxyde of iron a reddish brown precipitate, which has a somewhat lighter tint than that produced by pure potash,

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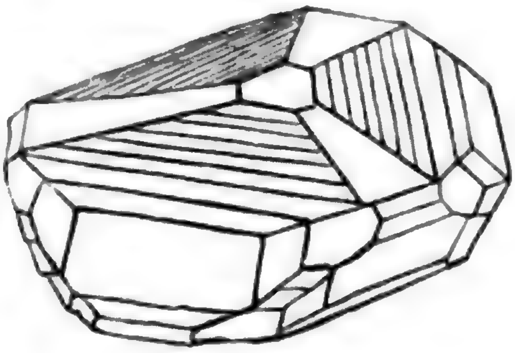
[1] According to W. Phillips, native oligist iron is of a deep steel grey colour, with a brilliant and often iridescent tarnish externally. It occurs lamellar and crystallised in many forms, which are derived from a slightly acute rhomboid. The general form of this substance, especially that from Elba, is as follows:—



or by ammonia. * This precipitate is a hydrate of peroxyde, which generally contains a little carbonic acid.

A solution of BICARBONATE OF POTASH determines in solutions of peroxyde of iron a light reddish brown precipitate, accompanied by a disengagement of carbonic acid. If the liquor be boiled, the disengagement of carbonic acid gas is more abundant, and the precipitate becomes darker[1].

A solution of CARBONATE OF AMMONIA behaves with ferric solutions like carbonate of potash[1].

A solution of PHOSPHATE OF SODA forms a white precipitate of neutral perphosphate of iron in neutral solutions of peroxyde of that metal. This precipitate turns brown by addition of ammonia, and after some time is completely dissolved by that alkali, provided an excess of phosphate of soda has been added. * The solution has a reddish brown colour. If, on the contrary, the solution of peroxyde of iron be in excess, the addition of ammonia precipitates a very basic perphosphate of iron mixed with peroxyde of iron, from which ammonia may take up a little phosphoric acid, but no peroxyde. This precipitate of perphosphate of iron is soluble in solution of carbonate of ammonia. A solution of carbonate of soda added to the precipitate of perphosphate of iron does not at first change the white colour of this persalt, but after some time it becomes reddish brown, and the perphosphate is then partly soluble in a large excess of carbonate of soda. On the contrary, pure potash immediately changes the colour of the perphosphate of iron into reddish brown, analogous to that of pure peroxyde of iron and takes up much phosphoric acid, but not all, and does not dissolve any portion of peroxyde of iron.

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[1] M. Wœhler has observed, that the hydrate of peroxyde of iron recently precipitated, is entirely soluble in carbonate of ammonia added in sufficient quantity. M. Berzelius in reporting this observation remarks, that the property which alkaline bicarbonates have of dissolving recently precipitated hydrate of peroxyde of iron has been long known, but that its solubility in carbonate of ammonia, to which the attention of chemistry had not hitherto been called, should induce them to abandon the use of this re-agent to precipitate peroxyde of iron. M. Berzelius, however, says, that whatever be the excess of carbonate of ammonia employed, the peroxyde of iron which it may have dissolved is *entirely* precipitated by diluting it with a sufficient quantity of water.—ED.

A solution of OXALIC ACID does not yield any precipitate with solutions of peroxyde of iron; the liquid only assumes a yellowish tinge.

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash) determines in solutions of peroxyde of iron, an immediate dark blue precipitate of Prussian blue, which is insoluble in muriatic acid[1]. [See note, page 85.]

A solution of FERRICYANURET OF POTASSIUM (red prussiate of potash) does not produce any precipitate in solution of peroxyde of iron, but the liquid then becomes a little darker in colour. * If, however, the liquor contains the least trace of protoxyde of iron, a blue precipitate is instantly produced[2].

* INFUSION OF GALLS produces in neutral solutions of peroxyde of iron a dark blue-black precipitate [ink], and if there be only traces of peroxyde of iron, the liquor becomes purple, but it must be as neutral as possible. A free acid dissolves the precipitate, and addition of ammonia added after the infusion of galls determines a precipitate of a reddish black colour.

HYDROSULPHURET OF AMMONIA determines in neutral solutions of peroxyde of iron, a black precipitate of sulphuret of iron which is insoluble in an excess of the re-agent[3]. The precipitate becomes oxydised in contact with the air and assumes a reddish brown colour. * When the quantity of peroxyde of iron is very minute, hydrosulphuret of ammonia gives the liquor a green colour, and the little sulphuret of iron which is suspended in the liquor is slowly deposited therefrom. This green colour, produced by hydrosulphuret of ammonia in a solution which contains only a minute trace of peroxyde of iron is a much more delicate characteristic of the presence of this latter substance than the precipitate of peroxyde of iron produced by ammonia. When ammonia has failed in giving a precipitate, a green colour may yet be produced by pouring hydrosulphuret of ammonia in the liquor.

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[1] If the solution of the persalt of iron be very dilute, and oxalic acid or an oxalate of potash be present, ferrocyanuret of potassium does not produce any precipitate of Prussian blue, because this substance is soluble in oxalic acid and in binoxalate of potash. This precipitate of Prussian blue is immediately decomposed by potash or soda, and peroxyde of iron is precipitated.—ED.

[2] According to Harting, ferricyanuret of potassium may detect $\frac{1}{440000}$ of protoxyde of iron.—ED.

[3] This precipitate of sulphuret of iron is also insoluble in alkalies and sulphurets of alkalies, but it dissolves easily in muriatic and in nitric acids.—ED.

SULPHURETTED HYDROGEN in solution or in the gaseous state, determines in both neutral and acid solutions of peroxyde of iron, a milky white precipitate, which is sulphur[1]. The liquor, after the expulson of the hydrogen, contains protoxyde of iron. * Aqueous solution of sulphuretted hydrogen produces a black precipitate of sulphuret of iron when poured in a neutral solution of peracetate of iron; but if the liquor contains any free acetic acid, a milky white precipitate of sulphur only is obtained[2].

* Acid solutions of persalts of iron have a yellow colour, which by boiling become reddish. Neutral solutions of persalts of iron have a reddish colour. If a small quantity of ammonia or of another alkali be poured in such a solution, a precipitate of hydrated peroxyde is indeed formed, but which disappears by stirring the liquor; the result is a basic persalt of iron, which is soluble, and the colour of which is redder than that of the neutral solution. But if the persalt of iron becomes basic by the addition of a larger quantity of alkali, it separates, and it is converted by an excess of alkali into hydrated peroxyde of iron.

* When the solution of a neutral or of a basic persalt of iron is boiled, the greater part of the peroxyde of iron is precipitated.

The persalts of iron, which are soluble in water, are decomposed by a red heat in contact with the air.

Neutral solutions of persalts of iron redden blue litmus paper.

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[1] This milky white turbidness is owing to the decomposition of the sulphuretted hydrogen, the hydrogen of which reduces the persalt to the state of the protosalt by taking up one-third of the oxygen of the persalt, with which it forms water, whilst the sulphur separates in the state of fine powder.—ED.

[2] The concentrated solutions of some persalts of iron, but especially those of perchloride and of persulphate of iron, receive a blood-red colour from the addition of sulphocyanic acid, and the soluble sulphocyanides, and such as sulphocyanide of potassium. This last re-agent is, according to Dr. Fresenius, the most delicate of all. Tincture of opium produces also a blood-red colour in solutions of persalts of iron. —ED.

The persalts of iron, which are insoluble in water, are soluble in muriatic acid, or in dilute sulphuric acid. If a solution of potash or of ammonia be added to such a solution, so as only just to supersaturate it, the insoluble compound is precipitated with its characteristic colour, and which, in most cases, is a white colour, as for example, in phosphate and arseniate of peroxyde of iron. But the greater the proportion of alkali added, and especially of potash, the more reddish brown the precipitate becomes. Hydrosulphuret of ammonia renders this precipitate instantly black, converting it into sulphuret of iron.

Before the BLOW-PIPE, the behaviour of persalts of iron resembles that of protosalts of iron.

Solutions of peroxyde of iron are most clearly distinguished from those of other bases by their behaviour with sulphuretted hydrogen, hydrosulphuret of ammonia, and ferrocyanuret of potassium. The use of these three tests easily identifies them.

All non-volatile ORGANIC SUBSTANCES prevent the complete precipitation of peroxyde of iron by alkalies, provided they be not in too large proportion. However a solution of ferrocyanuret of potassium, even in such cases, yields as yet a precipitate; and when the solution has previously been supersaturated with ammonia, which has failed to produce a precipitate, hydrosulphuret of ammonia will determine a black precipitate of sulphuret of iron.

* Certain organic substances, such as albumen, for instance[1], either render the precipitation of sulphuret of iron difficult, or even completely hinder it; in such a case the sulphuret remains suspended in the liquor and communicates a green colour to it.

The COMPOUNDS OF PROTOXYDE AND OF PEROXYDE OF IRON (*ferroso-ferric oxyde*) called common or octaedral magnetic iron ore ($FeO + Fe_2O_3$) are very common in nature. They are also formed when iron is heated red hot in contact with the air [the scales of iron at the smith's forge]. The first has always the same composition, but not the latter. All these combinations are black and strongly magnetic.

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[1] According to Dumas, quoted by Professor Brande, the serum of the blood, hot solutions of gelatin, starch, gum-arabic, starch sugar and diabetic sugar, glycerine, mannite, tartaric, citric, malic, mucic, kinic, and pectic acids produce the same effect.—ED.

To detect the presence of the two oxydes in these compounds, they are introduced with concentrated muriatic acid in a closed flask, and when dissolved a part of it is treated with an excess of an aqueous solution of sulphuretted hydrogen; the white precipitate thus produced, and which is sulphur, shows the presence of peroxyde of iron; another portion is now to be taken, diluted with water and solution of *ferricyanuret of potassium* added, which, if it produces a dark blue precipitate, indicates the presence of *protoxyde of iron*.

* Ferroso-ferric oxyde of iron is completely, though slowly, soluble in muriatic acid. It is precipitated from its solution in the state of a hydrate by ammonia and by the alkaline carbonates; the precipitate has a brown-black colour. If, however, a quantity of the re-agent only sufficient to precipitate the whole of the ferroso-ferric oxyde be added, and if the whole be well stirred, a precipitate of hydrated peroxyde of a pure reddish-brown colour is at first obtained, but which becomes black by a further addition of the re-agent. The ferroso-ferric hydrate is magnetic even whilst moist; in this state it is much more slowly converted into peroxyde of iron than the hydrated protoxyde. In the dry state it is unalterable in the air.

20. OXYDE OF CADMIUM, CdO.

(Oxyde cadumique.)

PURE oxyde of cadmium has a reddish-brown colour, at least when reduced to powder. It is neither fusible nor volatilizable by heat, but if mixed with organic substances or with pulverized charcoal it volatilizes, because it is then reduced into metallic cadmium, which is very volatile. Its hydrate is white, and absorbs a little carbonic acid by exposure to the air; when heated it loses its water, and assumes the reddish-brown colour of the oxyde. Both oxyde of cadmium and its hydrate are easily soluble in acids. Salts of cadmium are white.

A solution of POTASH produces in the solutions of the salts of cadmium, which are soluble in water, a white precipitate of hydrated oxyde of cadmium, insoluble in an excess of potash.

AMMONIA determines in neutral solutions of oxyde of cadmium a white precipitate of hydrate of oxyde of cadmium, which is very easily soluble in a slight excess of ammonia[1].

A solution of CARBONATE OF POTASH determines in solution of oxyde of cadmium a white precipitate of carbonate of cadmium, insoluble in an excess of the re-agent.

A solution of BICARBONATE OF POTASH likewise produces, in neutral solutions of oxyde of cadmium, a white precipitate of carbonate of cadmium, accompanied by a disengagement of carbonic acid.

A solution of CARBONATE OF AMMONIA produces in solutions of oxyde of cadmium, which may contain much muriate of ammonia, a white precipitate of carbonate of cadmium, insoluble in an excess of the re-agent[2].

A solution of PHOSPHATE OF SODA determines a white precipitate of phosphate of cadmium in neutral solutions of oxyde of cadmium.

A solution of OXALIC ACID poured in neutral solutions of oxyde of cadmium renders them immediately turbid. This precipitate, which is oxalate of cadmium, is easily soluble in pure ammonia.

A solution of FERROCYANURET OF POTASSIUM produces in solution of oxyde of cadmium a white precipitate of ferrocyanuret of cadmium, which has a very slight tinge of yellow, and which is soluble in muriatic acid.

A solution of FERRICYANURET OF POTASSIUM produces in solutions of oxyde of cadmium a yellow precipitate of ferricyanuret of cadmium, soluble in muriatic acid.

* INFUSION OF GALLS does not render neutral solutions of oxyde of cadmium turbid.

HYDROSULPHURET OF AMMONIA determines in neutral solutions of oxyde of cadmium a yellow precipitate of sulphuret of cadmium, insoluble in an excess of the re-agent, and unalterable in the air[1].

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[1] Berzelius says, when ammonia is poured upon pure anhydrous oxyde of cadmium it becomes at first white, and then it dissolves; and if the ammonia is driven off by evaporation, oxyde of cadmium is deposited in the state of a mucilaginous hydrate.—ED.

[2] Carbonate of ammonia, not having the power to dissolve oxyde of cadmium, is the re-agent employed for separating oxyde of cadmium from oxyde of zinc, which is soluble in carbonate of ammonia.—ED.

SULPHURETTED HYDROGEN, either in solution or in the gaseous state, produces a yellow precipitate of sulphuret of cadmium in alkaline and in acid solutions of oxyde of cadmium.

A rod of METALLIC ZINC precipitates metallic cadmium from its solutions in the state of grey shining spangles.

The salts of oxyde of cadmium, which are soluble in water, are decomposed by exposure to a red heat.

Neutral solutions of salts of cadmium redden litmus paper.

The salts of oxyde of cadmium, which are insoluble in water, are soluble in acids. It is very easy to recognise the presence of oxyde of cadmium in these acid solutions, by means of the yellow sulphuret which the solution, or a current of sulphuretted hydrogen gas determines therein.

Before the BLOW-PIPE salts of oxyde of cadmium may be detected, when, after mixing them with soda, they are heated upon charcoal in the interior flame; the charcoal becomes then covered with a reddish brown powder, which is oxyde of cadmium.

* If oxyde of zinc contains the smallest quantity of oxyde of cadmium, by exposing the compound for a few moments to the action of the reducing flame, in conjunction with a little soda, the presence of oxyde of cadmium becomes manifest, for the charcoal then, at a short distance from the assay, becomes covered with a powder of a dark yellow colour, which is better perceived after the charcoal has become cold. It is necessary to blow for a longer time in order to obtain a deposit of oxyde of zinc on the charcoal.

Solutions of oxyde of cadmium may be easily distinguished from those of the preceding bases by their deportment with solution of sulphuretted hydrogen, and with hydrosulphuret of ammonia.

The presence of non-volatile ORGANIC SUBSTANCES prevents oxyde of cadmium from being precipitated from its solutions by potash, but have no influence on the actions of the solutions of the alkaline carbonates.

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[1] It is a precipitate of a fine orange or reddish yellow colour, somewhat resembling orpiment, but distinct from it, because it is not flocculent, and easily falls at the bottom of the liquor.—ED.

21. OXYDES OF LEAD.

1° PROTOXYDE OF LEAD, PbO.

(*Oxyde plombique.*)

PURE protoxyde of lead is yellow, and its powder has a reddish tinge. (* By long exposure to the air it gradually absorbs carbonic acid, but without changing colour, and then it slightly effervesces with acids:) it easily melts at a dark red heat; and if it be melted in large quantities, it is scaly, and has an orange or a yellow colour; but its powder is reddish-yellow. In fusing it dissolves earths and metallic oxydes[1]. At a white heat it volatilises, especially with the contact of the air. When mixed with organic substances or charcoal powder it is easily reduced by heat. It is not quite insoluble in pure water, but it does not dissolve in water which contains minute traces of a salt of any kind. The best solvent of protoxyde of lead is nitric or acetic acid. When these acids fail in dissolving it completely, it is a proof that it is not pure. Commercial litharge often contains silicic acid, which remains undissolved after treatment with acids. * Salts of lead are colourless, they have an agreeable, sweet, and styptic taste.

A solution of POTASH produces in solutions of the soluble salts of protoxyde of lead a white precipitate of hydrated protoxyde, soluble in a pretty large excess of the re-agent, especially with the help of heat[2].

AMMONIA determines a white precipitate, insoluble in any excess of ammonia, and which consists ordinarily of a basic salt of protoxyde of lead, (a solution of acetate of lead is not troubled by ammonia, even though that solution be rather concentrated; but after some time, a basic acetate of lead is deposited[1].

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[1] It is owing to this property that the pots in which various metallic ores are smelted become damaged, and unfit for use when these ores contain oxyde of lead. —ED.

[2] According to Berzelius, 11 parts of potash and 13 of soda dissolve one part of protoxyde of lead.—ED.

A solution of CARBONATE OF POTASH produces in solution of protoxyde of lead a white precipitate of carbonate of lead, insoluble in an excess of the precipitant, soluble in pure potash.

A solution of BICARBONATE OF POTASH produces the same precipitate of carbonate of lead, but with disengagement of carbonic acid.

A solution of CARBONATE OF AMMONIA behaves with solutions of protoxyde of lead like those of carbonate of potash.

A solution of PHOSPHATE OF SODA forms in solutions of neutral salts of lead a white precipitate of phosphate of lead soluble in a solution of pure potash.

A solution of OXALIC ACID produces an immediate white precipitate of oxalate of lead in solutions of neutral salts of protoxyde of lead.

A solution of FERROCYANURET OF POTASSIUM produces a white precipitate of ferrocyanuret of lead in solutions of protoxyde of lead.

A solution of FERRICYANURET OF POTASSIUM produces no precipitate in lead solutions, because ferricyanuret of lead is soluble in water.

* INFUSION OF GALLS produces a dirty yellow precipitate in neutral solutions of protoxyde of lead.

HYDROSULPHURET OF AMMONIA produces a black precipitate of sulphuret of lead, insoluble in an excess of the re-agent.

* If the hydrosulphuret of ammonia employed be not recently prepared, and have a yellow colour, it may determine a reddish-brown precipitate, but which nevertheless becomes always black by standing. A solution of sulphuret of potassium, such as exists in common liver of sulphur[2] determines also a reddish-

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[1] This precipitate is a hexacetate of lead (acetate séplombique), composed of 6 atoms of oxyde of lead and 1 of acetic acid. It is purely astringent, not sweet, and sparingly soluble in cold water. At first the solution of acetate of lead is not precipitated by ammonia, because a soluble trisacetate of lead is formed, which passes into the state of a hexacetate only after some time has elapsed.—ED.

[2] Liver of sulphur, on account of its colour, was the name given formerly to the

brown precipitate in solutions of protoxyde of lead, and this precipitate turns black likewise by standing.

SULPHURETTED HYDROGEN dissolved in water or in the gaseous state, produces a black precipitate of sulphuret of lead in solutions of neutral and of acid salts of lead.

* When these solutions contain only an extremely feeble quantity of protoxyde of lead, aqueous solution of sulphuretted hydrogen produces a brown colour. If a solution of sulphuretted hydrogen, to which muriatic acid has been added, be poured in a solution of protoxyde of lead, taking care that the sulphuretted hydrogen does not predominate, a red or brownish-red precipitate is obtained, which however turns black spontaneously after some time. This precipitate becomes immediately black if a larger portion of the re-agent is used[1].

A rod of METALLIC ZINC plunged in solution of protoxyde of lead precipitates shining spangles of a blackish-grey colour, which are metallic lead[2].

Solutions of protoxyde of lead are likewise precipitated by a few re-agents which do not produce any precipitate in solutions of the oxydes of which we have hitherto treated.

Dilute SULPHURIC ACID and solutions of SULPHATES give in solution of oxyde of lead a white precipitate of sulphate of lead, which is almost insoluble in water, but which is taken up by a solution of potash. It is especially this precipitate which indicates the presence of oxyde of lead in solutions, because sulphuric acid produces compounds which are insoluble or sparingly soluble in dilute acids, with no other substances except baryta, strontia, lime, and oxyde of lead. Sulphate of lead differs from the earthy sulphates in this, that it is soluble

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compounds obtained by fusing potash or carbonate of potash with sulphur; or by the action of charcoal and heat upon sulphate of potash. The result is always a sulphuret, bisulphuret, or a persulphuret of potassium, according to the quantity of sulphur employed, mixed with hyposulphite of potash, which becomes converted into sulphate of that base.—ED.

[1] According to Mr. Harting, sulphuretted hydrogen may detect $\frac{1}{250000}$ of lead in solution.—ED.

[2] According to Mr. Harting, a bar of metallic zinc forms a sensible precipitate with $\frac{1}{5000}$ of lead.—ED.

in solution of potash, and especially because when moistened with hydrosulphuret of ammonia, it immediately turns black [which is not the case with the sulphates of baryta, lime, or strontia.] * This salt is soluble in hot *muriatic acid*, and the liquor on cooling deposits crystalline spangles of chloride of lead. Sulphate of lead is also slightly soluble in hot nitric acid, but the acid must not be dilute. The re-agents in which it is most soluble are the solutions of some salts, for instance, acetate of ammonia[1]. It is less soluble in dilute sulphuric acid than in any other vehicle[2].

MURIATIC ACID and solutions of METALLIC CHLORIDES produce in solutions of oxyde of lead, provided they be not too dilute, a white precipitate of chloride of lead, which redissolves by the simple addition of water. Ammonia produces in this solution of chloride of lead a white precipitate which is a compound of chloride and of oxyde of lead. The precipitate which is produced by muriatic acid and solutions of metallic chlorides is likewise soluble in potash.

* Chloride of lead is more soluble in pure water than in water which contains free muriatic acid, wherefore this acid precipitates it from its concentrated aqueous solutions[3].

A solution of IODIDE OF POTASSIUM determines in solutions of protoxyde of lead a yellow precipitate of iodide of lead, which is soluble in a large excess of the re-agent[4].

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[1] Sulphate of lead is also soluble in solutions of the acetates of potash and of soda. According to the experiments of Bischof, 1 part of sulphate of lead is soluble at a temperature of 53°. 6 Fahren., in 172 parts of nitric acid of sp. gr. 1·144; in 969 parts of solution of nitrate of ammonia, sp. gr. 1·29; in 47 parts of a solution of acetate of ammonia, sp. gr. 1·036. This property, which acetate of ammonia possesses of dissolving sulphate of lead, observes Berzelius, may be usefully resorted to for the purpose of separating sulphate of lead from other precipitates.—ED.

[2] According to Mr. Harting, sulphuric acid gives an appreciable precipitate in solutions which contain $\frac{1}{20000}$ of lead.—ED.

[3] One part of chloride of lead requires, according to Bischof, 135 parts of water for its solution. Chloride of calcium diminishes much the solubility of chloride of lead in water, wherefore it produces a precipitate in concentrated solutions of chloride of lead.—ED.

[4] This precipitate of iodide of lead has a fine lemon-yellow colour, and is also soluble in hot water, and slightly so even in cold water. According to Denot, 194 parts of boiling water, and 1235 parts of water at the ordinary temperature, dissolve

A solution of CHROMATE OF POTASH causes in solutions of protoxyde of lead a yellow precipitate of chromate of lead insoluble in dilute nitric acid, soluble in solution of pure potash. * Digested with ammonia, this yellow precipitate becomes of a reddish colour, because it becomes converted into bibasic chromate of lead[1].

The salts of lead, which are soluble in water, are decomposed when exposed to a red heat in contact with the air. Sulphate of lead, however, is not decomposed by a red heat.

Solutions of neutral salts of lead redden litmus paper.

Most of the salts of lead which are insoluble in water are soluble in nitric acid. When such a solution is not too acid and has not been diluted with too large a quantity of water, sulphuric acid determines a precipitate therein. Sulphate of lead is not soluble in dilute nitric acid, but it is easily recognised as a metallic salt, because by moistening it with hydrosulphuret of ammonia it turns black, and also because, treated before the blow-pipe with soda upon charcoal, metallic lead is very speedily reduced.

Before the BLOW-PIPE salts of lead are distinguished, because after being mixed with soda, and heated in the interior flame upon charcoal, they are very easily reduced into globules of metallic lead, which may be flattened by the hammer, and are not brittle, whilst the charcoal becomes covered with a yellow coating.

Solutions of protoxyde of lead are very easily distinguished from those of other oxydes, by their reaction with dilute sulphuric acid. They are distinguished from those of baryta, strontia, and lime, by their behaviour with hydrosulphuret of ammonia, and before the blow-pipe.

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one part of iodide of lead. On cooling, the solution made in boiling water deposits hexagonal sparkling scales of a fine golden colour, which are not altered by drying. If an insufficient quantity of iodide of potassium be added, so that the solution contains an excess of lead, the precipitate is of a very pale yellow colour.—ED.

[1] The ammonia combines with part of the chromic acid, and a subchromate of lead is the result. Chromate of potash, according to Mr. Harting, can detect $\frac{1}{70000}$ of lead in solution.—ED.

Though a solution of protoxyde of lead may contain many ORGANIC SUBSTANCES, and even be rendered quite dark by them, yet sulphuric acid precipitates protoxyde of lead therefrom. The presence of protoxyde of lead is detected in the precipitate by fusing it upon charcoal before the blow-pipe, in conjunction with soda. If the solution contains gum, sugar, or other like organic substances, the sulphate of lead is not easily deposited, but remains in suspension for a long time, and it is troublesome to gather upon a filter.

When the liquid thus mixed with a large quantity of organic matter contains only traces of protoxyde of lead, sulphuric acid yields no precipitate. In such a case, it is advisable to render the solution very slightly acid by addition of nitric acid, and to pass a current of sulphuretted hydrogen through it; by which means, the protoxyde of lead is completely precipitated in the state of sulphuret of lead: yet a pretty long time must elapse before the sulphuret has completely deposited. If the quantity of liquid is small, it is sufficient to pour in it an excess of solution of sulphuretted hydrogen, which precipitates the protoxyde of lead in the state of sulphuret, which is likewise to be melted by the blow-pipe upon charcoal, in conjunction with soda; by which means, metallic lead is obtained. When, on the contrary, protoxyde of lead is mixed with organic substances, in the solid or in the pasty state, it is best to mix the whole with carbonate of soda, and to expose it to a red heat in a hessian crucible; it is, however, necessary in doing this to avoid heating the mixture too strongly, which might volatilise the reduced lead. When the whole has cooled down, the melted mass is to be pulverised in an agate mortar with water, and the charcoal is to be carefully separated by levigation. The metallic lead remains in the mortar, and may then easily be recognised as such.

2°. RED LEAD—MINIUM.

[SUROXYDE PLOMBEUX.]

(*Probably* $2\,PbO + PbO_2$.)

THIS oxyde is pulverulent, and has a brick-red colour. When gently heated it turns black; but on cooling, it becomes red again. A stronger heat converts it into protoxyde of lead, and oxygen is disengaged. Nitric and acetic acids change its colour into brown, because it is thereby converted into peroxyde [Binoxyde of lead, PbO_2], which is brown, and remains undissolved, and into protoxyde of lead, which dissolves in the acid. Peroxyde of lead is also produced when this red oxyde of lead is treated by the aqueous solution of chlorine. If it be heated with muriatic acid, a chloride of lead is produced, accompanied by a disengagement of gaseous chlorine. Yet the first action of this acid in the cold way is to form a little peroxyde of lead. Potash has no action upon red lead.

* When red oxyde of lead is treated by nitric acid and organic substances, a little sugar for example, there is no peroxyde of lead formed; but, on the contrary, the red oxyde of lead becomes converted into protoxyde, which dissolves in the acid, and there is a disengagement of carbonic acid. Brick-dust, silica, and other substances, which may fraudulently be mixed with it, remain insoluble, and may easily be recognised.

Before the blow-pipe red oxyde of lead behaves like the protoxyde, into which it is in fact converted by the action of the heat.

3°. PEROXYDE OF LEAD, PbO_2.

[BINOXYDE OF LEAD.]

(*Suroxyde plombique.*)

THIS oxyde has a dark-brown colour, and is pulverulent. When heated, oxygen is disengaged, and it is then converted at once into protoxyde. When treated with muriatic acid, it is converted, even in the cold way, into chloride of lead, and gaseous chlorine is given off.

Before the blow-pipe its deportment is the same as that of protoxyde of lead.

Note by E. Peligot:—

SUBOXYDE OF LEAD, Pb_2O.

[OXYDE PLOMBEUX.]

* The recent experiments of M. Pelouze, which confirm and extend those of Messrs. Dulong and Boussingault, have demonstrated beyond doubt the existence of a suboxyde of lead [Pb_2O] containing less oxygen by half than protoxyde of lead [PbO.]

* That oxyde is obtained pure by heating oxalate of lead to about 300° cent., 572° Fahr. Pending all the time of the operation, a mixture of carbonic acid and oxyde of carbon is disengaged, in which these gases exist in the ratio of 1 of oxyde of carbon to 3 of carbonic acid.

* Suboxyde of lead has sometimes a dingy, at other times a velvety deep black colour.

* It is converted by nitric, sulphuric, muriatic, and acetic acids into metallic lead and into protoxyde of lead, with which these acids enter into combination.

* It undergoes the same decomposition by treatment with alkalies.

* Mixed with a small quantity of water, in contact with the air, much heat is evolved, there is absorption of oxygen from the atmosphere, and the result is a white powder, which is the ordinary hydrated protoxyde.

* Exposed to a low red heat, suboxyde of lead is decomposed, forming a mixture of metallic lead and of protoxyde of lead; the lead may then be dissolved by mercury, which has no action on the protoxyde.

22. OXYDE OF BISMUTH, BiO.

[OXYDE BISMUTHIQUE.]

PURE oxyde of bismuth is yellow, its colour becomes darker when heated, but on cooling it re-assumes its original hue. Exposed to a strong heat it fuses into a glass, which after cooling is yellow. It is not volatile[1]. When heated with organic substances, or with pulverised charcoal, it is easily reduced into metallic bismuth. Acids dissolve it readily. Many salts of bismuth are soluble in water, but not completely, because they are decomposed by water into an acid salt, and a basic salt, the first of which is dissolved, whilst the second being insoluble in water renders it milky. When a sufficient quantity of nitric or of muriatic acid is added, the solution is completely effected, and the liquor is then clear.

* The decomposition of nitrate of bismuth into an acid salt, and a sub-salt, takes place when about twenty or thirty parts of water are added; if the quantity of water be more considerable, a large quantity of the basic salt is redissolved, nay the solution may be rendered complete by abundance of water. The basic chloride of bismuth, which results from the decomposition of chloride of bismuth by water is completely insoluble in that fluid, and can be dissolved only by adding a sufficient quantity of an acid. It is owing to the insolubility of sub-chloride of bismuth, that not only solutions of chloride of sodium, and of other metallic chlorides, as well as small portions of muriatic acid, produce a precipitate in very dilute aqueous solutions of basic nitrate of bismuth; however, when a larger proportion of these re-agents is added, the precipitate is re-dissolved. Alcohol dissolves chloride of bismuth without decomposing it.

A solution of POTASH yields in solutions of oxyde of bismuth a white precipitate of hydrate of bismuth insoluble in an excess of the re-agent.

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[1] Berzelius says, that bismuth is volatisable at a high heat, and may be distilled in close vessels, and then sublimes in foliated crystals.—ED.

AMMONIA behaves in the same manner.

A solution of CARBONATE OF POTASH produces a white precipitate of carbonate of bismuth, also insoluble in an excess of the re-agent.

A solution of BICARBONATE OF POTASH produces a similar precipitate; but carbonic acid is disengaged.

A solution of CARBONATE OF AMMONIA behaves in the same manner.

A solution of PHOSPHATE OF SODA determines a white precipitate of phosphate of bismuth.

A solution of OXALIC ACID does not produce an immediate precipitate; but after a certain time a crystalline precipitate of oxalate of bismuth is formed.

A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash) produces a white precipitate of ferrocyanuret of bismuth insoluble in muriatic acid.

A solution of FERRICYANURET OF POTASSIUM (red prussiate of potash) determines a pale-yellow precipitate of ferricyanuret of bismuth soluble in muriatic acid.

* INFUSION OF GALLS produces a yellow precipitate in solutions of oxyde of bismuth.

HYDROSULPHURET OF AMMONIA forms a black precipitate of sulphuret of bismuth which, when in small quantity, is very dark brown. It is insoluble in an excess of the re-agent.

SULPHURETTED HYDROGEN, either gaseous or liquid, determines a black precipitate of sulphuret of bismuth, which becomes manifest even in acid solutions. When the solution contains only a small quantity of oxyde of bismuth, the precipitate is dark-brown. Sulphuret of bismuth is very easily reduced into the metallic state, when, after having mingled it with soda, it is heated upon charcoal in the interior flame of the blow-pipe.

A rod of METALLIC ZINC plunged in solutions of oxyde of bismuth precipitates bismuth in the metallic state, under the form of a black spongy mass. This effect is produced even in solutions which have become milky from the addition of water.

Solutions of bismuth may be also distinguished by the following re-agents :—

A solution of IODIDE OF POTASSIUM produces a brown precipitate of basic iodide of bismuth very soluble in an excess of the re-agent.

A solution of CHROMATE OF POTASH determines a yellow precipitate of chromate of bismuth soluble in dilute nitric acid[1].

Salts of oxyde of bismuth are decomposed by exposure to a red heat in contact with the air.

Solutions of salts of oxyde of bismuth, which can only be solutions of acid salts, redden litmus paper.

The salts of bismuth, which are insoluble in water, are soluble in acids. These solutions, especially that in muriatic acid, become milky by the addition of water, provided the quantity of acid which has been employed to dissolve it has not been too considerable. Solution of sulphuretted hydrogen in water produces in them a dark-brown or black precipitate, which, treated before the blow-pipe upon charcoal with soda is easily reduced into a globule of bismuth.

Before the BLOW-PIPE, salts of oxyde of bismuth are readily recognised, because after being mingled with soda they may most easily be reduced in the interior flame into metallic globules, which are brittle, and may be broken to pieces under the hammer, whilst the charcoal becomes covered with a yellow coating [of oxyde] similar to that produced when salts of oxyde of lead are treated in the same manner.

Salts of oxyde of bismuth are easily recognised by their behaviour with hydrosulphuret of ammonia, and with water, especially when the latter contains a little muriatic acid, or solution of a metallic chloride. They differ from salts of oxyde of lead by their reaction with solution of potash, and also because dilute sulphuric acid produces no precipitate in solutions of oxyde of bismuth. The globules of bismuth reduced by the blowpipe are distinguished from those of lead by their brittleness.

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[1] This yellow precipitate of chromate of bismuth differs from chromate of lead, which yields also a yellow precipitate by chromate of potash in this, namely :—

Chromate of bismuth is *soluble* in dilute nitric acid, *insoluble* in potash ;
Chromate of lead is *insoluble* in do. do., *soluble* in do.—ED.

The presence of non-volatile organic substances, even that of tartaric acid, does not hinder the precipitation of solutions of oxyde of bismuth by water and the alkalies[1].

Note by E. Peligot, in the French edition :—

PEROXYDE OF BISMUTH Bi_2O_3.

[SESQUIOXYDE OF BISMUTH.]

(Suroxyde Bismuthique.)

* BESIDES the oxyde described by Mr. H. Rose, we must admit a peroxyde of bismuth, the existence of which has been placed beyond doubt by the experiments of MM. A. Stromeyer, Jacquelain, and Frémy.

* This last chemist observed, that when oxyde of bismuth is heated with soda it absorbs oxygen, and is transformed into *bismuthate* of soda; if this salt be then boiled with an excess of soda, the metallic oxyde becomes dehydrated, and abandons the alkali with which it was combined. The oxyde thus obtained has a brown colour, similar to that of peroxyde of lead, and it may be washed with pure concentrated nitric acid, without undergoing decomposition. According to M. Frémy its composition is represented by $Bi_2\ O_4$, that of oxyde of bismuth being $Bi_2\ O_3$.[2]

* This same peroxyde had already been obtained by Mr. A. Stromeyer by boiling the oxyde of bismuth obtained from the calcination of subnitrate of bismuth with a solution of chlorite of soda; this oxyde of bismuth, which is yellow, gradually

assumes a deeper tinge during the operation. As it is difficult to peroxydise the last portions, it is necessary, after having separated and washed the black powder, to digest it in dilute nitric acid, which dissolves the portions of oxyde which have escaped peroxydisement.

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[1] This is owing to the insolubility of the precipitated subsalt of bismuth in tartaric acid, which establishes a distinction between the precipitates produced by water in solutions of oxyde of antimony, and which are soluble in tartaric acid, as will be seen subsequently, page 185.—ED.

[2] These atomic formulas are incorrect, and are founded upon the equivalent which was formerly adopted for bismuth, and which was corrected by M. Lagerhjelon. Oxyde of bismuth contains 1 atom of each element, and its formula is therefore BiO. The peroxyde is composed of 2 atoms of bismuth, and 3 of oxygen; it is therefore a sesquioxyde, and its formula therefore $Bi_2\ O_3$.—ED.

* Peroxyde of bismuth is decomposed by a temperature of 400° cent. [about 752° Fahr.] into oxyde of bismuth and oxygen. Treated by concentrated acids, oxygen is disengaged even at the ordinary temperature[1]. Treated by muriatic acid, chlorine gas is evolved, and a chloride of bismuth is formed.

23. OXYDES OF URANIUM, UO.

1° PROTOXYDE OF URANIUM.

(Oxyde Uraneux.)

* PURE protoxyde of uranium is of a dark greyish-black colour when it has been obtained by calcining the peroxyde of uranium, precipitated by ammonia, and subsequently digesting it in muriatic acid; but when it is finely pulverised it is green. It is almost insoluble in muriatic acid. Sulphuric acid diluted with a very small quantity of water dissolves it, with the help of heat, and produces a green liquid. It is very soluble in nitric acid: this solution, however, contains also some peroxyde of uranium.

* The solution of protoxyde of uranium in sulphuric acid behaves as follows with the re-agents below:—

* A solution of POTASH produces a voluminous brown precipitate of hydrate of protoxyde, insoluble in an excess of the re-agent.

* AMMONIA forms a brownish-black precipitate of hydrate of protoxyde of uranium, insoluble in an excess of the re-agent. After a very long time the uppermost portions of the precipitate become yellow, because they are converted into peroxyde of uranium.

* A solution of CARBONATE OF POTASH determines a dirty

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[1] Dilute acids, with the help of heat, produce also a disengagement of oxygen.—ED.

greenish precipitate of protocarbonate of uranium, soluble in a large excess of the re-agent.

* A solution of BICARBONATE OF POTASH produces the same effect, only the precipitate is more soluble in an excess of the re-agent.

* A solution of CARBONATE OF AMMONIA behaves in the same manner.

* A solution of PHOSPHATE OF SODA causes a dirty whitish-green precipitate of protophosphate of uranium, provided the solution does not contain too much free acid.

* A solution of OXALIC ACID soon determines, even in very acid solutions of protoxyde of uranium, a dirty light-yellowish green precipitate of oxalate of uranium.

* A solution of FERROCYANURET OF POTASSIUM produces a brown-red precipitate.

* A solution of FERRICYANURET OF POTASSIUM does not produce any immediate precipitate, but after a time a brown-red precipitate appears.

* HYDROSULPHURET OF AMMONIA determines, in solutions of protoxyde of uranium, which have been neutralised as exactly as possible, a black precipitate of sulphuret of uranium, which is easily collected, and which is insoluble in an excess of the re-agent. The supernatant liquid owes its yellow colour only to the excess of the re-agent used.

* SULPHURETTED HYDROGEN, either liquid or gaseous, produces no precipitate.

* Before the BLOW-PIPE protoxyde of uranium behaves like the peroxyde (page 112).

* The best method of distinguishing solutions of protoxyde of uranium from those of other substances consists in converting the protoxyde of uranium into the peroxyde of that metal by means of nitric acid, and then to test it by the re-agents which will be presently treated of. Protoxyde of uranium in the solid state is very easily detected by means of the blow-pipe.

* Non-volatile ORGANIC SUBSTANCES prevent protoxyde of uranium from being precipitated by alkalies.

2°. PEROXYDE OF URANIUM, U_2O_3.

[SESQUIOXYDE OF URANIUM.]

(*Oxyde Uranique.*)[1]

* PEROXYDE of uranium recently precipitated has a yellow colour. Exposed to a red heat it is converted into protoxyde of uranium, and then it has a dark-greenish black colour. The portion of peroxyde which has not been reduced may be extracted from the ignited mass by treatment with muriatic acid. When peroxyde of uranium has been precipitated from its solution by either potash or soda, or when ammonia has been employed to precipitate it from a solution which contained either those alkalies, or alkaline earths, the precipitate, after calcining, is orange-red, and it is composed of these fixed bases and of peroxyde of uranium chemically combined together, and which, in this state, the action of a red heat cannot convert into protoxyde of uranium. Peroxyde of uranium is easily soluble in acids, and its solution behaves towards re-agents as follows:—

* A solution of POTASH produces a yellow precipitate of uraniate of potash, insoluble in an excess of alkali.

* AMMONIA behaves in the same manner, only the precipitate is, of course, uraniate of ammonia.

* A solution of CARBONATE OF POTASH determines a yellow precipitate of carbonate of peroxyde of uranium soluble in an excess of the re-agent: a yellow precipitate is also formed after some time in this last solution.

* A solution of BICARBONATE OF POTASH produces a yellow precipitate of carbonate of peroxyde of uranium, which is very soluble in an excess of the re-agent, and from which solution no peroxyde of uranium is precipitated after some time.

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[1] M. Jacquelain obtained pure sesquioxyde of uranium by decomposing nitrate of uranium by a temperature of 250 or 300° cent. (from 482 to 572° Fahr.) as follows:—After having deprived the nitrate of its water and of part of its acid by the direct action of fire, it is to be reduced to powder, and heated in a bath of oil or of fusible alloy in closed tubes of glass or of china.—Pure sesquioxyde of uranium is yellow, with a tinge of brown. It is soluble without residuum in most diluted acids; its solutions are yellow.—PELIGOT.

* A solution of CARBONATE OF AMMONIA behaves in the same manner.

* A solution of PHOSPHATE OF SODA produces in solutions of peroxyde of uranium, provided they do not contain too much free acid, a white precipitate of phosphate of uranium: this precipitate has a very slight tinge of yellow.

* A solution of FERROCYANURET OF POTASSIUM determines a brownish-red precipitate.

* A solution of FERRICYANURET OF POTASSIUM produces no precipitate.

* INFUSION OF GALLS produces a dark brown precipitate in neutral solutions of peroxyde of uranium.

* HYDROSULPHURET OF AMMONIA poured in solutions of peroxyde of uranium, which contain no excess of acid, produces a brown precipitate of sulphuret of uranium, which is not sensibly dissolved by an excess of the re-agent: the supernatant liquid at first appears black, but after some time the precipitate is completely deposited.

* SULPHURETTED HYDROGEN, either aqueous or gaseous, produces no precipitate in solutions of peroxyde of uranium.

* The salts of peroxyde of uranium, which are soluble in water, are decomposed by a red heat in contact with the air.

* Solutions of neutral salts of peroxyde of uranium redden blue litmus paper.

* Nearly all the salts of peroxyde of uranium, which are insoluble in water, are dissolved by muriatic acid. Some of them, for example, the phosphate of peroxyde of uranium, resemble so much the pure peroxyde, that analyses have been made in which the presence of the acid combined with it has been overlooked. The best is to dissolve the combination of peroxyde of uranium in muriatic acid, to supersaturate the solution thus obtained with ammonia, and to add hydrosulphuret of ammonia. The precipitate is then to be digested in muriatic acid, and the filtered liquid contains protoxyde of uranium in solution. The liquid which has been filtered from the sulphuret of uranium, contain the acid with which the peroxyde of uranium was combined.

* Before the BLOW-PIPE peroxyde of uranium and its salts may

thus be detected: namely, that dissolved in microcosmic salt upon a wire of platinum it communicates to the exterior flame a yellowish colour strongly tinged with green, which, on cooling, augments to such an extent that it then appears green only. In the interior flame the colour is green. When peroxyde of uranium has been dissolved in borax upon the bent end of a wire of platinum, the colour of the exterior flame is distinctly yellow, and in the interior flame, green. Protoxyde of uranium behaves with the blow-pipe like peroxyde of uranium.

* Theyellow colour of the precipitate, which pure alkalies and alkaline carbonates produce in solutions of peroxyde of uranium, and their behaviour towards hydrosulphuret of ammonia, are so characteristic that they cannot be confounded with the bases which have been treated of in the preceding pages.

* When a solution of peroxyde of uranium contains much non-volatile ORGANIC MATTER, more especially tartaric acid, peroxyde of uranium is not precipitated by alkalies.

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* Note by E. Peligot in the French edition:—

Within the last few years, uranium has been the object of particular study, and the result of the labours of various chemists upon this body render it necessary that the preceding notions upon the oxydes of uranium should be completed or rectified.

* It is now known that the substance uranium (*urane*), which had until lately been considered as an element, is a metallic oxyde. Uranium, the true metal, which is prepared by decomposing chloride of uranium by means of potassium, is easily distinguished from all other metals by its peculiar combustibleness. It is not much changed by exposure to the air at the ordinary temperature, notwithstanding its prevalent form, but it burns with extreme brilliancy, and a very white light, when heated to incipient redness. Thus, by shaking upon a lighted taper a few particles of this metal, they form brilliant sparks in the heated atmosphere, which surrounds the flame.

* Uranium forms five or six combinations with oxygen. Protoxyde of uranium and peroxyde of uranium are the only com-

pounds of that metal which can combine with acids to form salts.

* 1° *Suboxyde of uranium* U_4O_3 [the equivalent of uranium being 750, oxygen = 1; or 60 hydrogen = 1]. This oxyde is produced when the aqueous solution of subchloride is treated by ammonia. At the moment of precipitation it is brown, but the colour is altered almost instantly into a greenish yellow colour, because it becomes oxydized at the expense of the water, whilst hydrogen is disengaged. After some time, this new oxyde, which has not as yet been isolated, becomes brown, and ultimately yellow, under the influence of the air and of the excess of ammonia; it is then transformed into uraniate of ammonia.

* 2° *Protoxyde of uranium* UO. This oxyde was until lately mistaken for the metal itself. Its colour and aspect varies, according to the process by which it has been obtained.

* When it is obtained from the reduction of an oxyde, or of a salt, by means of hydrogen gas, it is of a cinnamon or marone colour. When in a state of minute division it is phosphorescent, it burns with a weak light, and is transformed into a black powder.

* When this oxyde has been obtained from the reduction of the double chloride of uranium and potassium, by hydrogen gas, or simply by calcining this salt with muriate of ammonia, it is in the form of crystalline black shining spangles, which, however, appear somewhat translucid when viewed through the microscope.

* Protoxyde of uranium, prepared in the dry way, is not acted upon by muriatic and diluted sulphuric acids, even when hot. Concentrated sulphuric acid, however, and likewise nitric acid, dissolve it, and this last acid produces nitrate of peroxyde of uranium [*nitrate uranique*].

* The characters which were formerly attributed to solution of protoxyde of uranium, in dilute sulphuric acid, belong properly to the sulphate and other salts of protoxyde of uranium. This oxyde, in effect, constitutes the green salts of uranium; in the state of hydrate it is reddish brown; it is soluble in diluted acids, and produces green solutions, which ultimately become yellow

in contact with the air, because they become converted into persalts of uranium.

* A green solution of a salt of protoxyde of uranium gives, after some time, with nitrate of silver, a precipitate of metallic silver, and a yellow salt of peroxyde of uranium is the result.

* When treated by nitrate of silver, the protoxyde of uranium obtained from calcining the yellow oxalate in close vessels, or by the reduction of the green oxyde, by means of sulphur, produces a yellow precipitate of nitrate of silver, and silver in the metallic state.

* *Binoxyde of uranium*, or *black oxyde of uranium*, U_4O_5. This oxyde is obtained by calcining persulphate or pernitrate of uranium at a high temperature.

* Put in contact with acids, it does not combine with them integrally, and gives a mixture of salts of proto and of peroxyde of uranium.

* It may, in effect, be considered as composed of two equivalents of protoxyde, and one of peroxyde of uranium ($2\ UO + U_2O_3$).

* *Tritoxyde of uranium*, or *olive oxyde*, U_3O_4, is also a compound of proto and of peroxyde ($UO + U_2O_3$). It is obtained by submitting the preceding oxyde to incipient red heat, in contact with oxygen or with the air.

* The colour of tritoxyde of uranium is dark olive. Treated by concentrated sulphuric acid under the influence of a gentle heat it furnishes a greenish yellow mixture of the sulphates of both oxydes. By heating the mixture more strongly, sulphurous acid is disengaged, and sulphate of peroxyde of uranium is formed. This sulphate has a light yellow colour.

* *Peroxyde of uranium* (oxyde uranique, U_2O_3). Until lately this oxyde had never been obtained in a pure state. It is known that by treating solutions of peroxyde of uranium by alkalies, the precipitate thus formed always retains a certain quantity of the precipitate which cannot be disengaged by washing.

* Mr. Ebelmen has shown that the hydrated peroxyde of uranium may be obtained by exposing a solution of oxalate of peroxyde of uranium to solar light; after some time, a violet-brown flocculent precipitate is deposited, which thrown upon a

filter and exposed to the air is rapidly converted into a lemon-coloured product, which is hydrate of peroxyde of uranium.

* This hydrate is transformed by a gentle heat into anhydrous peroxyde of a brick-red colour; subjected to a higher temperature, it is converted into green oxyde.

Peroxyde of uranium is easily soluble in acids, and its salts have the characters which have been previously mentioned.—E.P.

24. OXYDES OF COPPER.

1°. SUBOXYDE OF COPPER, Cu_2O.

[*Formerly* PROTOXYDE[1] OF COPPER.]

(*Oxyde Cuivreux.*)

* SUBOXYDE of copper, as it is found in nature, is of a copper-red colour. When in powder it resembles the colour of pulverised cochineal. It is unalterable in the atmosphere, but when heated in contact with it, it becomes converted into protoxyde of copper; if, however, it be heated in close vessels, it undergoes no change provided the temperature be not too high. It is converted by dilute sulphuric and other acids into metallic copper, which separates, and protoxyde of copper which dissolves in the acid employed. Muriatic acid is the only one which,

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[1] This oxyde was until lately called protoxyde of copper, the equivalent being then reckoned to be 64. But a careful examination of the binary compounds of that metal and the composition of its salts and oxydes has induced modern chemists to adopt 32 as the atomic weight of that metal. This number is besides justified, because, according to the law discovered by Dulong and Petit, that the specific heat of simple bodies is inversely as their atomic weight, the product of the multiplication of the specific heat of copper by the atomic number, gives 30·368; a number much nearer 32 (the chemical atomic weight or equivalent now adopted) than 64, which was formerly determined upon. On the other hand, Professor Faraday discovered another law, that the specific electricity of different substances being also inversely as their atomic weights, the calculated specific electricity of copper gives nearly 32; and again, the specific gravity of copper gives 32 as its chemical equivalent, Gay Lussac having observed that the metals which have a specific gravity above 9 or varying from 10 to 20, have all atomic weights above 96, whilst the atomic weights of those whose density is below 9, that is between 1 and 9, is about 30, and seldom exceeds 32. Taking therefore 32 as the equivalent of copper, the protoxyde and protochloride of copper are now regarded as suboxyde and subchloride, the atomic symbol being Cu_2 O, and Cu_2 Cl, instead of CuO and CuCl, and the deutoxyde and deutochloride of copper are now regarded as protoxyde and protochloride, and marked CuO and CuCl, instead of CuO_2, and $CuCl_2$ as formerly.—ED.

poured in excess upon suboxyde of copper, forms a solution of a subsalt, which, in the present case, is a subchloride of copper. The solution has a brown colour, which is owing to a small quantity of protochloride, for when the solution does not contain any portions of this latter salt, it is colourless; by exposure to the air it is gradually converted into solution of protochloride, and ultimately assumes a green colour. When less muriatic acid is employed, suboxyde of copper is converted into a white powder, which is subchloride of copper. If a suitable quantity of water be added to a solution of subchloride in an excess of muriatic acid, a white powder of subchloride of copper is precipitated. Solution of subchloride of copper behaves as follows towards re-agents:—

* A solution of POTASH poured in small quantity in that solution, saturates the free acid which it contains, and the consequence is a precipitate of subchloride of copper in the state of a white powder, for this salt is soluble only in free muriatic acid.

A great quantity of potash determines a brownish yellow precipitate, which is hydrate of suboxyde, and which is not dissolved by an excess of the re-agent. When this precipitate remains for a very long time exposed to the air, it becomes gradually of a brownish black colour, and the suboxyde is converted into protoxyde of copper.

An excess of AMMONIA poured in solution of subchloride of copper, would form with it a colourless liquid, were the operations performed out of the contact of the air; but ordinarily the liquid becomes of a light blue colour, because the presence of the air immediately induces the formation of a little protochloride of copper. When this solution is left exposed to the air, it becomes in a short time of a dark blue colour. This colouring manifestly begins at the surface, which generally is dark blue, whilst the rest is as yet only of a light blue colour. A solution of potash poured in a solution of subchloride of copper to which ammonia has been added, produces therein a brownish yellow precipitate of hydrated suboxyde, provided the quantity of ammonia thus added be not too considerable in proportion to the potash.

* A solution of CARBONATE OF POTASH produces a yellow precipitate of subcarbonate of copper in suboxyde solutions of copper.

* A solution of BICARBONATE OF POTASH acts in the same manner.

* A solution of CARBONATE OF AMMONIA behaves like pure *ammonia;* but there is an effervescence produced owing to a disengagement of carbonic acid.

* A solution of PHOSPHATE OF SODA produces in solutions of suboxyde of copper which are not too acid, a white precipitate of phosphate of suboxyde of copper, which in time absorbs the oxygen of the air, and becomes greenish blue.

* A solution of OXALIC ACID determines in solutions of suboxyde of copper a white precipitate of oxalate of suboxyde of copper, which by long standing becomes greenish blue.

* A solution of FERROCYANURET OF POTASSIUM (yellow prussiate of potash), gives a white precipitate, which, if left in contact with the air, becomes reddish brown in a very short time.

* A solution of FERRICYANURET OF POTASSIUM determines an immediate reddish brown precipitate.

* HYDROSULPHURET OF AMMONIA produces in the solutions of suboxyde of copper which have been saturated with ammonia, a black precipitate of sulphuret of copper insoluble in an excess of the re-agent.

* A solution or a current of SULPHURETTED HYDROGEN produces a brown precipitate of sulphuret of copper in solutions of suboxyde of copper.

* A solution of IODIDE OF POTASSIUM gives a white precipitate of subiodide of copper, and the supernatant liquid contains no free iodine.

* The subsalts of copper which are soluble in water, are decomposed when exposed to a red heat in contact with the air.

* Most of the subsalts of copper which are insoluble in water are soluble in free muriatic acid. The suboxyde of copper contained in such solution may easily be converted into protoxyde of copper by treating it with nitric acid. It will be seen further

on, (page 122), what means should be resorted to in order to detect its presence in the solution under examination.

* Before the BLOW-PIPE suboxyde of copper behaves like protoxyde of copper, the only difference being that, when dissolved with borax or microcosmic salt, it immediately communicates to the exterior flame a dirty brown colour which, with the protoxyde, is manifested only in the interior flame.

2° PROTOXYDE OF COPPER, CuO.

[*Formerly* DEUTOXYDE OF COPPER.]

(*Oxyde Cuivrique.*)

PROTOXYDE of copper is pulverulent black, and requires a very strong heat for fusion. If heated with charcoal or with organic bodies it is easily reduced either into suboxyde of copper or into metallic copper. It is very soluble in acids, even after having been ignited. The solution has ordinarily a blue colour. The muriatic acid solution is emerald green. Hydrate of protoxyde of copper is blue; being strongly dried at the temperature of boiling water, it parts with its water and becomes black.

* Protosalts of copper are blue or green when they contain water of crystallisation; anhydrous protosalts of copper have a white colour and a few are brown.

A solution of POTASH determines in solutions of protoxyde of copper a voluminous blue precipitate of hydrate of protoxyde of copper, which becomes black when boiled with an excess of potash, because protoxyde of copper is deposited, which easily subsides to the bottom of the vessel. When a solution of protoxyde of copper is boiled with a less proportion of solution of potash than is necessary to produce a complete decomposition, instead of a black, a light greenish precipitate is obtained which is a basic salt of protoxyde of copper.

A small quantity of *ammonia*, poured in solutions of protoxyde of copper, determines a greenish precipitate, which is a basic salt of protoxyde of copper, very easily soluble in an excess of ammonia, producing a blue liquor[1]. The blue colour of the liquid is of a much deeper hue than that obtained by solution of protoxyde of nickel in an excess of ammonia; even when the quantity of protoxyde of copper is very small, the blue colour produced by ammonia is much darker than that of protoxyde of nickel[1]. Even when the quantity of protoxyde of copper is so small that the solution appears colourless, ammonia at once renders it blue. A cold solution of pure potash poured in a cold ammoniacal solution of protoxyde of copper does not immediately produce any precipitate, but after some time a blue precipitate of hydrate of protoxyde is formed, provided the solution be not too dilute. Yet when the ammoniacal solution of protoxyde of copper is made to boil with a solution of potash, a heavy black precipitate of protoxyde of copper is produced, and after it has quite deposited at the bottom of the vessel, the liquid which before was of a dark blue colour is quite colourless.[2]

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[1] This blue liquor is due to the solution of the basic double salt of ammonia and

A solution of CARBONATE OF POTASH in the cold produces in solutions of protoxyde of copper a blue precipitate of carbonate of protoxyde of copper, which, by boiling, becomes black and is easily deposited[3].

A solution of BICARBONATE OF POTASH determines a light greenish precipitate, which an excess of the precipitate redissolves, producing a light blueish liquid.

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copper; for example, the ammonio-subsulphate of copper formed by supersaturating a solution of sulphate of copper with ammonia (the *cupreum ammoniacale* of pharmacy) which may be obtained in the solid state by careful evaporation, and which is very soluble in water, to which it imparts again the same splendid blue colour.—ED.

[1] The ammoniacal solutions of nickel are immediately precipitated by potash in the state of an apple-green hydrate of protoxyde of nickel, whilst the ammoniacal solution of copper is not precipitated by potash, at least immediately.—ED.

[2] To account for this precipitate, it should be recollected that pure hydrate of protoxyde of copper is not soluble in ammonia, or in other words, the blue solutions obtained by pouring an excess of ammonia in solution of copper are solutions of compounds of a basic double salt of copper and ammonia; by pouring potash in such an ammoniacal solution, the acid of the salt combines with the potash, and protoxyde of copper is accordingly precipitated, notwithstanding the presence of ammonia, since protoxyde of copper is not soluble in it.—ED.

[3] This precipitate, according to Dr. Fresenius, is a hydrated basic carbonate of copper ($CuO, CO_2 + CuO, HO$,) which upon boiling is converted into black protoxyde of copper.—ED.

A solution of CARBONATE OF AMMONIA poured in small quantity produces a light greenish precipitate, which is a basic salt of protoxyde of copper, which a larger quantity of the reagent re-dissolves; the liquid then appears as blue as the solution of protoxyde of copper to which caustic ammonia has been added. Boiled with a solution of pure potash a heavy black precipitate of protoxyde of copper is also formed.

A solution of PHOSPHATE OF SODA produces in solutions of protoxyde of copper a greenish white precipitate of phosphate of protoxyde of copper, soluble in ammonia, and thus giving a blue liquor in which a solution of potash determines, by boiling, a black heavy precipitate of protoxyde of copper.

A solution of OXALIC ACID forms an immediate greenish white precipitate of oxalate of copper, in neutral solutions of protoxyde of copper.

A solution of FERROCYANURET OF POTASSIUM produces, in solutions of protoxyde of copper, a reddish brown precipitate of ferrocyanuret of copper insoluble in muriatic acid[1].

A solution of FERRICYANURET OF POTASSIUM produces a greenish yellow precipitate of ferricyanuret of copper, likewise insoluble in muriatic acid.

* INFUSION OF GALLS produces no precipitate in solutions of protoxyde of copper, provided they contain no iron.

HYDROSULPHURET OF AMMONIA produces, in neutral solutions of protoxyde of copper, a black precipitate of sulphuret of copper, which appears of a dark brown colour when in small quantity, and which is insoluble in an excess of the precipitant[2], and also in ammonia.

An aqueous solution or a current of sulphuretted hydrogen gas produces in either neutral or acid[3] solutions of protoxyde of copper a black precipitate of sulphuret of copper, which, when in small quantity, appears dark brown.

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[1] Ferrocyanuret of potassium is a very delicate test for copper in clear solutions; at least $\frac{1}{20000}$ of metallic copper may be thus rendered visible.—ED.

[2] Sulphuret of copper is very slightly soluble in hydrosulphuret of ammonia; but it is altogether insoluble in sulphuret of potassium and of sodium, either of which should be selected in preference for the purpose of completely separating sulphuret of copper from the sulphurets of other metals.—ED.

[3] If the liquid is very strongly acid, it should first be diluted with water before testing with sulphuretted hydrogen.—ED.

A rod of METALLIC ZINC precipitates protoxyde of copper from its solutions in the form of a black coating.

A rod of METALLIC IRON precipitates protoxyde of copper as metallic copper, and with its peculiar colour. Very minute traces of copper may thus be precipitated from their solutions by a rod of polished iron, which becomes covered with a red film of copper[1].

Solutions of protoxyde of copper may likewise be recognised by the following re-agents:—

A solution of IODIDE OF POTASSIUM produces a white precipitate of iodide of copper, the colour of which can be well ascertained only after having separated it from the liquid which is coloured by free iodine. This precipitate is soluble in an excess of the re-agent.

A solution of CHROMATE OF POTASH forms in solutions of protoxyde of copper, a reddish brown precipitate of chromate of copper, which, when ammonia is added, is easily dissolved, and produces a liquid of an emerald-green colour. This precipitate is also very soluble in dilute nitric acid.

The salts of protoxyde of copper, which are soluble in water, are decomposed by exposure to a red heat. Sulphate of copper, however, is not thus decomposed, provided the heat be not too strong.

Solutions of neutral salts of protoxyde of copper redden litmus paper.

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[1] If the solution of protoxyde of copper be concentrated, the copper falls down immediately in the form of a powder, but in dilute solutions the copper is deposited more or less slowly according to the degree of dilution, but always in a film which perfectly covers the iron, and makes it look like a blade or bar of copper. Instead of iron only, a foil of platinum and one of iron may be immersed in the liquid to be tested, and which should be very slightly acid. Muriatic acid is preferable, and the two bars on being brought into direct contact, copper if present will be deposited in the state of a red film of metallic copper on the platinum foil; or a few drops of the solution slightly acidulated may be placed upon platinum foil, and a piece of clean iron wire plunged through the drops so as to touch the platinum, which will become covered with a film of copper at the point in contact with the drops of liquid if any copper be present. Instead of iron wire, one of zinc may be used. By this means $\frac{1}{150000}$ of copper may be detected.—ED.

The salts of protoxyde of copper, which are insoluble in water, are soluble in free acids. The most minute portions of protoxyde of copper may be detected in these solutions by precipitating it in the state of sulphuret of copper, by means of sulphuretted hydrogen, and testing the precipitate with the blow-pipe. The acid solutions of these combinations become blue when an excess of ammonia is added, exactly like the other salts of copper; a quantity of ammonia less than sufficient to saturate the acid, precipitates the insoluble salt of copper from the solution.

Salts of protoxyde of copper are very easily detected by means of the blow-pipe. Dissolved in borax or in microcosmic salt they form in the exterior flame a bead of a fine green colour, and in the interior flame, a bead of a dirty reddish brown colour. When the quantity of the salt of protoxyde of copper is very minute, the reddish brown colour is easily determined by the addition of tin.[1]

* When the test is carried on with borax, without addition of tin, or when there is only a small quantity of peroxyde of copper, the glass heated in the interior flame often becomes transparent and of a ruby colour. When the quantity of protoxyde of copper is too large, a portion of it is reduced in the metallic state both with borax and with salt of soda.

Mixed with soda and heated in the interior flame upon charcoal, copper is reduced from these salts; the most minute traces may thus be recognised, after washing the charcoal away, by the characteristic colour of the particles of the reduced copper.

Solutions of *protoxyde of copper* may easily be recognised by their behaviour with ammonia, ferrocyanuret of potassium, and hydrosulphuret of ammonia. They are distinguished from solutions of nickel by their deportment towards a solution of potash and of sulphuretted hydrogen.

* Several ORGANIC SUBSTANCES, when contained in solutions of protoxyde of copper, may cause the reduction of part of the

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[1] Berzelius remarks, that if, after having added the tin, the operator should blow too strongly, the copper will be precipitated in the metallic state, especially with microcosmic salt, and the colouring of the glass is destroyed.—ED.

copper in the metallic state, especially by boiling; sugar more particularly produces that effect. But in neutral solutions this reduction is always very slow, and never complete; yet, in most cases, it takes place more rapidly, as well as more completely, in presence of free alkalies.

The deportment of solutions of protoxyde of copper is singularly modified by the presence of NON-VOLATILE ORGANIC SUBSTANCES. When they are not too abundant, and provided the liquid is only slightly coloured by them, an excess of potash produces no precipitate, but the liquid then assumes a blue colour, similar to that produced by caustic ammonia[1]. This is the case for example, when white wine, solution of sugar, or of tartaric acid contains a sufficient quantity of sulphate of copper, of verdigris, or of another salt of copper. The more abundant protoxyde of copper is in the solution, the deeper is the blue colour produced. When this alkaline solution of copper is boiled, the protoxyde of copper, in most cases, is reduced, and a precipitate of hydrated suboxyde of a brown yellow colour is formed, which, however, is often reddish brown. Sometimes the copper is thus almost entirely precipitated in the state of hydrated suboxyde. This is the case for example, when white wine, which has been adulterated with a salt of copper, is treated as above. In many cases, however, the liquid remains blue after boiling, and then a small quantity only of the copper is precipitated in the state of suboxyde of copper, as for example, when the solution operated upon is one of sugar containing protoxyde of copper; and sometimes the blue liquid is not in the slightest degree altered by boiling, as for example amongst others, the solutions of protoxyde of copper, which contain tartaric acid. When these liquids contain traces only of protoxyde of copper, solution of potash cannot detect it; for in such a case, the liquid does not become blue, and even by boiling no precipitate of suboxyde of copper is formed. Neither can solution of potash develop the blue colour when the liquid contains so much organic matter as to be of a very dark hue, which is the case with red wine to which much protoxyde of copper has been added. An opaque solution of a dirty green is then produced, and a precipitate of the same colour falls down; but by boiling, a reddish brown precipitate of suboxyde is formed.

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[1] Animal substances, such as albumen, glue, &c., communicate a lilac colour, but vegetable substances, such as starch, gum, sugar, &c., communicate a blue colour.—Ed.

In order to produce, by ammonia, a blue colour in solutions of protoxyde of copper containing non-volatile organic substances, it is necessary that the protoxyde of copper be sufficiently abundant, and that the liquid be not very dark. When white wine, for instance, contains a pretty considerable portion of protoxyde of copper, it becomes dirty green or brown by the addition of an excess of ammonia; it is only when the protoxyde of copper held in solution is very abundant, that caustic ammonia determines a blue colour in the liquid. When the copper solution, owing to the presence of organic substances, has a very dark colour, an excess of ammonia does not render it blue, even though it may contain a pretty considerable quantity of protoxyde of copper. A red wine, which contains protoxyde of copper, becomes dirty brown only by addition of ammonia, which is a change similar to that produced in pure red wine by ammonia.

One of the re-agents most to be depended upon for promptly detecting protoxyde of copper in liquids which contain much non-volatile organic matter, is solution of ferrocyanuret of potassium. When a liquid contains a considerable quantity of organic substances, mixed with only extremely minute traces of protoxyde of copper, ferrocyanuret of potassium determines therein the same reddish brown precipitate as in the pure solutions of protoxyde of copper; it is necessary, however, that the solution should be neutral or slightly acid, but not alkaline. By this re-agent extremely minute traces of protoxyde of copper may be rendered apparent in white wine, solutions of sugar, and other solutions of organic substances, provided they have not a dark colour. In dark liquids, for example in red wine, ferrocyanuret of potassium cannot detect protoxyde of copper, unless the quantity be very considerable.

The safest method to detect the slightest traces of protoxyde of copper in a solution is to precipitate it in the metallic state by means of bright iron, for example, by the blade of a knife. The only requisite condition is, that the liquid thus tested be neutral, or at any rate but very feebly acid. * If it be strongly acid, much hydrogen gas is evolved, which pushes as it were the precipitated zinc off its surface; in consequence of which, when the protoxyde of copper is not abundant, the copper coating, which is the characteristic test, and a delicate one, is not formed. In the same manner when the liquid operated upon contains all sorts of organic substances, and is very dark, nay, completely opaque[1], the least portion of protoxyde of copper is shown by the pellicle of red metallic copper which enfilms the iron.

If the liquid contains only a very small quantity of protoxyde of copper, several hours are required for the production of this coating of copper upon the iron. This test is even more delicate than sulphuretted hydrogen; for the aqueous solution of sulphuretted hydrogen, poured in solutions containing only a minute portion of protoxyde of copper mingled with a large quantity of organic substances, or hydrosulphuret of ammonia added to alkaline solutions of the same substance, betrays, it is true, the presence of protoxyde of copper by a brown, but not by a black, colour. In order, however, to acquire the entire conviction of the presence of protoxyde of copper it is necessary to collect on a filter the sulphuret of copper thus precipitated, and to test it with the blow-pipe, in order to establish that it contains copper. Now it is difficult, sometimes impossible, to separate minute quantities of sulphuret of copper by filtration, because it remains for a very long time suspended in liquids which contain much organic matter in solution; besides, it often occurs that solution of sulphuretted hydrogen fails in indicating extremely minute traces of dissolved copper, whilst clean iron will as yet determine a precipitate of metallic copper in these solutions. In a word, when a liquid is very dark, solution of sulphuretted hydrogen cannot be resorted to to determine whether it contains any dissolved protoxyde of copper.

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[1] For example, writing ink which contains sulphate of copper, a substance detrimental to the quality of that liquid, being tested with the blade of a knife, will be covered so as to appear changed into a blade of copper.—Ed.

When organic substances in the solid or in the pasty state are found mixed with small portions of protoxyde of copper they are generally to be digested in dilute nitric acid, or likewise, in some cases, in dilute sulphuric acid, and the filtered liquor may then be tested for protoxyde of copper. But extremely minute traces of this oxyde cannot thus be detected when mixed with a large quantity of organic matter; the best is then to mix the mass with carbonate of soda or of potash, and to expose the whole to a red heat in a hessian crucible; after which the ignited mass may be pulverised, the charcoal is removed by washing, and the traces of reduced copper remain in the crucible. In this way copper may be detected in food the cooking of which has been performed in copper utensils, and in bread which has been adulterated with small quantities of sulphate of copper.

The method and precautions which, according to Jacquemyns, should be adopted for the purpose of positively demonstrating the existence of the minutest trace of copper are the following:

Dilute the substance with enough water to form a soft paste, to which add double its weight of crystallised carbonate of soda in powder. Introduce the mixture in a hessian crucible, and after putting the cover on, heat it gradually, and maintain it for a quarter of an hour at a low red heat. After cooling, pulverise the charred mass in an agate mortar. To effect this, take only a portion of the mass, moisten it with water, and carefully rub it so as to dilute it, and then pour more water in the mortar, moderately rubbing the whole with the pestle, then attentively pour the water off which is mixed with the charcoal; pulverise again the mass which is left behind, and again wash the charcoal off until none of it is left; this done, small metallic and shining spangles are found in the mortar which have the colour of copper. If in this operation less carbonate of soda than stated is employed, the protoxyde of copper, it is true, is also reduced; but it is then in such a state of division that there is danger of washing it off with the charcoal. It is likewise necessary to take care that the crucible should be made red hot, because this is also a means of better agglomerating the particles of reduced copper. In order to avoid the danger of a portion of the alkaline carbonate penetrating the bottom of the crucible and fusing it, the best is to take a certain quantity of the substance to be analysed, and to deposit it at the bottom of the crucible unmixed with the alkaline carbonate. A mortar of agate must be used: one of porcelain or of stone-ware should not be substituted.

* According to Kuhlman, the best method to determine small quantities of protoxyde of copper in bread which has been poisoned with a protosalt of copper, consists in incinerating about [200 grammes] 3000 grains of such a bread in a platinum capsula. The ashes are then transferred to one of porcelain, a quantity of nitric acid is to be poured upon them, so as to bring the mass to the consistency of cream, and heat is applied until the greatest part of the free acid is volatilized. The mass is then to be digested in water, and filtered. The protoxyde of copper dissolved by the nitric acid may then be easily detected in the filtered liquor. To accomplish this, Kuhlman proposes solution of ferrocyanuret of potassium, or hydrosulphuret of ammonia, first supersaturating the liquor with ammonia, and filtering when the latter re-agent is to be employed. But it is better to dilute the solution with a proper quantity of water to form a precipitate of sulphuret of copper by means of a current of sulphuretted hydrogen; and, lastly, to examine this sulphuret with the blowpipe.

* The reducing of the bread to ashes, as prescribed in this method, is a very tedious operation. It may be expedited however by making use of extremely shallow and wide platinum capsulas, so as freely to admit the air during the combustion.

* A good method of summarily examining white bread, which is suspected of being poisoned by a salt of copper, consists in moistening the bread with solution of ferrocyanuret of

potassium, which will impart a pink colour to the bread if it contain any protoxyde of copper. If the bread to be so tested were brown, the change of colour would be too slight to be perceived.

25. OXYDE OF SILVER, AgO.

(Oxyde Argentique.)

In the pure state, oxyde of silver is a powder of a brownish grey colour, which solar light turns black, and is reduced into metallic silver, with disengagement of oxygen gas when exposed to a red heat. Oxyde of silver is very soluble in nitric acid, and in a few other acids.

* Salts of silver are colourless, but they turn black in the light of the sun; when sheltered from its influence they remain white.

A solution of POTASH produces in solutions of oxyde of silver a light brown precipitate of oxyde of silver insoluble in an excess of potash, but which is dissolved by ammonia[1].

A very small quantity of AMMONIA poured in neutral solutions of silver determines a brown precipitate of oxyde of silver, which is immediately, and very easily dissolved by a larger portion of ammonia. When the solution of oxyde of silver contains a free acid, no precipitate is formed by saturating it with ammonia. A solution of oxyde of silver, to which an excess of ammonia has been added, yields a precipitate when treated by solution of pure potash, provided the excess of ammonia be very slight.

A solution of CARBONATE OF POTASH produces in solutions of oxyde of silver a white precipitate of carbonate of silver soluble in ammonia.

A solution of BICARBONATE OF POTASH determines a white precipitate of carbonate of silver soluble in ammonia.

A solution of CARBONATE OF AMMONIA produces a white precipitate of carbonate of silver soluble in an excess of the re-agent.

A solution of PHOSPHATE OF SODA produces in neutral solutions of oxyde of silver a yellow precipitate of basic phosphate of silver soluble in ammonia: the supernatant liquor reddens litmus paper. If the phosphate of soda be strongly ignited before the experiment, and then dissolved in water, its solution produces in those of oxyde of silver a white precipitate of neutral phosphate of silver soluble in ammonia, and the supernatant liquor is neutral.

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[1] The presence of ammoniacal salts, either partially or entirely, prevent the formation of this precipitate.—Ed.

A solution of OXALIC ACID determines in neutral solutions of oxyde of silver a white precipitate of oxalate of silver, soluble in ammonia.

A solution of FERROCYANURET OF POTASH produces a white precipitate of ferrocyanuret of silver.

A solution of FERRICYANURET OF POTASH determines a brownish-red precipitate of ferricyanuret of silver, which has a great resemblance with that produced by ammonia in solutions of persalts of iron.

* INFUSION OF GALLS produces no precipitate in solutions of oxyde of silver—after some time, but more rapidly with the help of heat, the liquor deposits metallic silver in the state of a black powder, or else the sides of the vessel become coated with a black metallic pellicle.

HYDROSULPHURET OF AMMONIA yields a black precipitate of sulphuret of silver insoluble in an excess of the re-agent and in ammonia[1].

SULPHURETTED HYDROGEN, either in aqueous solution, or in the gaseous state, gives a black precipitate of sulphuret of silver in neutral acid, or ammoniacal solutions of oxyde of silver.

A bar of METALLIC ZINC precipitates silver from its solutions in the metallic state: near the zinc the reduced silver is black; but at a certain distance from it, it is white.

The following re-agents may also be resorted to for testing solutions of oxyde of silver.

MURIATIC ACID, and solutions of METALLIC CHLORIDES produce a precipitate of chloride of silver, even in very dilute solutions of silver. When the solution contains only extremely minute portions of oxyde of silver, the precipitate is slowly deposited, and the liquor has an opalescent hue[1]; if the quantity be more abundant, this precipitate has a curdy flocculent appearance. It is insoluble in dilute acids. * Concentrated muriatic acid dissolves a little of it, especially with the help of heat; but upon adding water all that which had dissolved is again precipitated. Ammonia dissolves the precipitate of chloride of silver, but it is reproduced by supersaturating the ammoniacal solution with a dilute acid. Exposed to the sunshine, the precipitate soon loses its white colour, and the surface becomes grey, or rather purple.

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[1] This precipitate of sulphuret of silver is also insoluble in other alkaline sulphurets and in alkalies, and likewise in cyanide of potassium and dilute acids. But boiling concentrated nitric acid, says Dr. Fresenius, decomposes and dissolves it, and sulphur is separated.—ED.

* It is, however, sufficient to mix it with a little protochloride of mercury to render it unalterable by sunlight.

A solution of IODIDE OF POTASSIUM produces in solutions of oxyde of silver a white precipitate having a yellow tinge, and which is iodide of silver. This precipitate is only very sparingly soluble in ammonia[2]; but when so treated, the colour becomes pure white;—it is more soluble in an excess of a solution of iodide of potassium, * and is insoluble in dilute nitric acid.

A solution of CHROMATE OF POTASH gives at first a crimson red precipitate of chromate of silver, which becomes reddish-brown, and is soluble in dilute nitric acid, in ammonia, and in a large quantity of water.

A solution of PROTOSULPHATE OF IRON determines a white precipitate of metallic silver in neutral solutions of oxyde of silver.

A solution of PROTOCHLORIDE OF TIN, to which enough muriatic acid is added to render it clear, produces a white precipitate of chloride of silver, when poured in small quantity in a solution of oxyde of silver. If a larger quantity of protochloride of tin is employed, the silver is reduced and precipitated in the state of a dark brown powder of a very small bulk.

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[1] When the precipitate has subsided, which takes place after a time, the supernatant liquid is clear.—ED.

[2] According to Martini, 2500 parts of ammonia of sp. gr. 0·960 are required to dissolve one of iodide of silver.—ED.

The white or light-coloured precipitates of silver are most peculiarly distinguished by the rapidity with which their surface assumes a black colour when exposed to solar light in a moist state. Of all these precipitates, that produced in solutions of oxyde of silver by muriatic acid and the metallic chlorides, is the most easily altered by the influence of light; and, on the contrary, this change of colour is trifling or null in those precipitates which are produced by iodide of potassium and phosphate of soda.

The salts of oxyde of silver which are soluble in water are decomposed by exposure to a red heat.

The solutions of the neutral salts of silver have no action upon litmus paper.

Almost all the salts of silver which are insoluble in water are soluble in nitric acid, and the presence of silver can be detected in such a solution by means of muriatic acid, which produces a white curdy precipitate of chloride of silver, insoluble in acids.

Before the BLOW-PIPE, the salts of silver are very speedily reduced into metallic silver, when fused in conjunction with soda. That character renders them easy of detection. * Dissolved in borax, or in microcosmic salt, in the exterior flame they give an opalescent glass.

Solutions of silver are easily recognized by the precipitate which muriatic acid determines in them, and which differs from all others in this—that it is soluble in ammonia, and insoluble in dilute acids[1].

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[1] Chloride of silver, after being fused, has a horny appearance, which in fact was the cause of the name horn-silver, by which it was formerly known. The first effect of the action of heat is to give it a pink colour, and then at a temperature below redness, it fuses into a yellowish transparent liquid, which on cooling becomes white, and is so soft that it can be cut with a knife. Exposed to a white heat in open vessels, it volatilises in thick heavy white fumes. The precipitate with muriatic acid is therefore quite characteristic; the only metals which this acid can precipitate are oxyde of silver, suboxyde of mercury, and oxyde of lead, but that of silver is the only one which is soluble in ammonia, and muriatic acid is so delicate a test, that one part of silver may be detected by it in 113 million parts of water. According to Pfaff, it almost ceases to produce a perceptible reaction when the solution is diluted with 227 million parts of water.—ED.

The presence of organic substances does not prevent muriatic acid from forming a precipitate in solutions of oxyde of silver[1].

26. OXYDES OF MERCURY.

[1°. SUBOXYDE OF MERCURY, Hg_2O.][2]

(*Oxyde Mercureux.*)

* PURE suboxyde of mercury is black. It is reduced by a very gentle heat into metallic mercury and protoxyde of mercury (red oxyde). A stronger heat reduces the protoxyde, but the ultimate result is metallic mercury and oxygen gas. It is also very often converted into metallic mercury and protoxyde of mercury by the action of several acids, especially if a free alkali be present. The best method to obtain a solution of suboxyde of mercury consists in treating an excess of the metal by nitric acid. The neutral subsalts of mercury are white. When basic, they often have a yellowish colour. Some of them dissolve only partially in water, by which they are decomposed into an acid salt, which the water takes up, and into a basic salt, which remains insoluble. This is the case, for example, with the neutral nitrate of suboxyde of mercury[3].

Solutions of suboxyde of mercury behave with re-agents as follows :—

A solution of POTASH produces a black precipitate of suboxyde of mercury, insoluble in an excess of the precipitant.

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[1] Mr. Levol has indicated a very simple method to reduce chlorate of silver into metallic silver, which consists in dissolving sugar in a solution of caustic potash, and pouring it upon chloride of silver, and boiling the whole. In a short time the sugar reduces the silver, carbonic acid gas is evolved, and after washing, the silver is obtained in a pulverulent state.—ED.

[2] This is again taking the equivalent of mercury to be 100, instead of 200, as formerly. The reasons for this change are the same as have been alluded to in the note on suboxyde of copper, page 115. Accordingly, the compounds known formerly as protoxyde and protochloride (calomel), are now called suboxyde and subchloride, and the binoxyde and bichloride (sublimate) are now regarded as the protoxydes and protochlorides of mercury.—ED.

[3] According to Berzelius, the neutral nitrate of suboxyde of mercury, Hg_2O, NO_5, is soluble *without decomposition* in a small quantity of hot water. It is only when a large quantity of water is used that it is decomposed into a soluble acid salt, and an insoluble basic salt, which decomposition however does not take place when the liquid contains a little free acid.—ED.

AMMONIA produces also a black precipitate, insoluble in an excess of the re-agent[1].

A solution of CARBONATE OF POTASH produces a dirty yellow precipitate, which turns black by boiling, and which is soluble in a great excess of alkaline carbonate.

A solution of BICARBONATE OF POTASH produces a white precipitate of carbonate of suboxyde of mercury, which turns black by boiling, and disengages carbonic acid.

A solution of CARBONATE OF AMMONIA produces a grey precipitate when poured in small quantity, but in large quantity the precipitate is black.

A solution of PHOSPHATE OF SODA gives a white precipitate of phosphate of suboxyde of mercury.

A solution of OXALIC ACID gives also a white precipitate of oxalate of suboxyde of mercury.

A solution of FERROCYANURET OF POTASSIUM gives a white gelatinous precipitate of ferrocyanuret of mercury.

A solution of FERRICYANURET OF POTASSIUM produces a reddish-brown precipitate of ferricyanuret of mercury, which after a time becomes white.

* INFUSION OF GALLS produces a light yellowish precipitate.

HYDROSULPHURET OF AMMONIA determines an immediate black precipitate of sulphuret of mercury, insoluble both in an excess of the re-agent and in ammonia; soluble in solution of pure potash, but with a residuum forming a black powder, which is metallic mercury, and which may be recognized as such when, after collecting it upon a filter, it is rubbed with a glass rod, and viewed through a magnifying glass. If the filtered alkaline liquid be supersaturated with an acid, a black precipitate of sulphuret of mercury is formed.

SULPHURETTED HYDROGEN, either liquid (aqueous solution) or gaseous, determines an immediate black precipitate of sulphuret of mercury, in neutral or in acid solutions of suboxyde of mercury. The precipitation takes place even when much less sulphuretted hydrogen gas is employed than is necessary to completely decompose the subsalt of mercury.

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[1] The black precipitate produced by ammonia is a double salt of ammonia and suboxyde of mercury.—ED.

A rod of METALLIC ZINC precipitates mercury in the metallic state, in the form of a grey film, which is an amalgam of zinc.

Solutions of suboxyde of mercury may also be recognized by means of the following re-agents:—

MURIATIC ACID and solutions of METALLIC CHLORIDES produce, even when as small a quantity as possible is poured in solutions of suboxyde of mercury, a white precipitate of subchloride of mercury, insoluble in simple acids[1], and which addition of ammonia turns black.

A solution of IODIDE OF POTASSIUM determines a greenish-yellow precipitate of iodide of mercury, which a large addition of the re-agent renders black, and in an excess of which it is soluble.

A solution of CHROMATE OF POTASH gives a red precipitate of chromate of mercury[2].

A drop of a solution of suboxyde of mercury placed upon a piece of bright COPPER, and which, after a little time, is rubbed with paper, leaves upon the copper a silvery mark, which disappears when made red hot[3].

The salts of suboxyde of mercury, which are soluble in water, are volatilised and decomposed at a red heat.

* The same occurs with most of the combinations of suboxyde of mercury which are insoluble in water. Subchloride and subbromide of mercury are volatilisable without decomposition.

Solutions of salts of suboxyde of mercury redden litmus paper.

Most of the salts of suboxyde of mercury which are insoluble in water are soluble in dilute nitric acid. Muriatic acid determines in these acid solutions a white precipitate of subchloride of mercury, insoluble in ammonia, but which is turned black by it.

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[1] Subchloride of mercury is soluble with difficulty, and very slowly, in muriatic and in nitric acids by a long continued ebullition. The result being with the first, the production of perchloride of mercury and metallic mercury, which is left insoluble. The second acid converts it into perchloride and pernitrate of mercury. Caustic potash, as well as ammonia, converts the white subchloride into black suboxyde of mercury.—ED.

[2] The colour of this red (orange-red) precipitate is more or less intense, according to the degree of concentration of the liquor or quantity of the re-agent used.—ED.

[3] Protochloride of tin poured in solutions of suboxyde of mercury, produces a grey precipitate of metallic mercury, which may be agglomerated into globules by agitation, or by boiling with muriatic acid. Protoxyde of mercury behaves in the same manner with this re-agent, as will be seen, page 142.—ED.

When salts of suboxyde of mercury are mixed with dry soda, or other bases, in a glass tube, closed at one end, and therein heated to redness by the blow-pipe, mercury sublimes in the form of a grey coating, in which globules of mercury most distinctly appear when touched with a glass rod. The minutest portions of a salt of suboxyde of mercury may thus be detected.

* When, however, subchloride or subbromide of mercury are submitted to this treatment with well-dried soda, a considerable portion may be volatilised without decomposition. In order to avoid this mishap, it is necessary to moisten the mixture very slightly before applying the heat.

Solutions of salts of suboxyde of mercury are very easily detected by their behaviour with muriatic acid, the precipitate produced by this re-agent being insoluble in dilute acids, and blackened by ammonia, a character which quite distinguishes it from that produced by muriatic acid in solutions of oxyde of silver. In the dry way, the presence of mercury can very easily be ascertained by the production of globules of that metal.

2°. PROTOXYDE OF MERCURY, HgO.

[*Formerly* PEROXYDE OF MERCURY.]

(*Oxyde mercurique.*)

PURE protoxyde of mercury is ordinarily in a crystalline state, and then it has a brick-red colour; it becomes yellowish when reduced into very fine powder.

* It is not entirely insoluble in water[1]. When this oxyde is heated, it acquires a black colour, but becomes brick-red again on cooling. A stronger heat decomposes it into oxygen gas and metallic mercury.

* When long exposed to light, it becomes black at the surface.

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[1] According to Donovan, when protoxyde of mercury is boiled in distilled water, a single drop of dilute caustic ammonia produces a slight turbidness, which is owing to the formation of an insoluble compound of protoxyde of mercury and ammonia.—ED.

When adulterated with red lead, the fraud may be detected by heating it in a small glass tube, closed at one end until the protoxyde of mercury is completely decomposed, there will be a residuum of fused protoxyde of lead; or if brick dust is the adulterating ingredient, upon treating the mixture as above, the brick dust is left unchanged behind.

Protoxyde of mercury is very soluble in acids.

* The adulteration with red lead may also be detected, because the solution in nitric acid leaves a precipitate of brown oxyde of lead (page 102). The neutral salts of mercury are colourless; the basic ones often have a yellowish colour.

A solution of POTASH determines in solutions of protoxyde of mercury a yellow precipitate of hydrate of protoxyde of mercury, insoluble in an excess of the re-agent. When too small a quantity of potash is poured in the liquid, the precipitate has a tinge verging upon reddish-brown, and it consists of a basic salt. If the solution of protoxyde of mercury contains any muriate of ammonia, *potash* produces a white precipitate, which has the same composition as that produced by ammonia in solutions of protochloride of mercury (sublimate)[1]. If the solution contains much free acid, and only a small proportion of protoxyde of mercury, an excess of potash produces no precipitate, or only a slight one, after a time.

AMMONIA produces a white precipitate[2], insoluble in an excess of the re-agent.

A solution of CARBONATE OF POTASH determines a reddish-brown precipitate, insoluble in an excess of the re-agent, and the colour of which is not thus altered; it consists of a basic salt of protoxyde of mercury. When a solution of protochloride of mercury (sublimate) has been precipitated by carbonate of potash, the precipitate consists of a combination of protoxyde and of protochloride of mercury. If the solution of protoxyde of mercury [red oxyde] contains muriate of ammonia, solution of carbonate of potash produces a white precipitate, which has the same composition as that formed by ammonia, when poured in solutions of protochloride of mercury (sublimate)[1].

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[1] The precipitate produced in solutions of corrosive sublimate by an excess of potash, soda, or ammonia, is a yellow hydrate of protoxyde of mercury. But if salts of ammonia be present, the precipitate is white, and is a subsalt of mercury combined with the ammoniacal compound.—ED.

[2] The white precipitate produced by ammonia in solutions of protochloride of mercury (sublimate), was formerly called simply *white precipitate of mercury*. It is the Hydrargyri ammonio-chloridum of pharmacy.—ED.

A solution of BICARBONATE OF POTASH produces a reddish-brown precipitate in solutions of sulphate, and in those of nitrate of protoxyde of mercury, at the same time carbonic acid is disengaged. This precipitate is a basic salt. A solution of protochloride of mercury (sublimate) is not troubled at first by that of bicarbonate of potash; but after some time a dark reddish-brown precipitate is deposited.

A solution of CARBONATE OF AMMONIA produces in solutions of protoxyde of mercury a white precipitate, the constitution of which is the same as that which ammonia determines in the same solutions.

A solution of PHOSPHATE OF SODA gives a white precipitate of phosphate of mercury in those of sulphate and of nitrate of protoxyde of mercury, but added to those of protochloride of mercury (sublimate) a very slight turbidness only is occasioned.

A solution of OXALIC ACID produces a white precipitate of oxalate of mercury in those of sulphate and nitrate of protoxyde of mercury, and none in those of protochloride (sublimate.)

A solution of FERROCYANURET OF POTASSIUM produces in solutions of protoxyde of mercury a white precipitate, which by long standing acquires a blue tinge, owing to the formation of prussian blue, cyanide of mercury remains dissolved in the liquid.

A solution of FERRICYANURET OF POTASSIUM produces a yellow precipitate in those of sulphate and nitrate of protoxyde of mercury, but none in those of protochloride of mercury (sublimate.)

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[1] M. Duflos has shown that the composition of the precipitate produced by carbonate of soda in a mixture of corrosive sublimate and of muriate of ammonia, is quite different from that produced by ammonia in solution of corrosive sublimate. The precipitate formed by carbonate of soda contains 12·29 per cent. of muriate of ammonia, 62·66 per cent. of protochloride of mercury (sublimate), and 25·05 of protoxyde of mercury; the formula would therefore be $(HgCl_2 + N_2H_8Cl_2) + (Hg_2Cl_2 + Hg_2O)$; that is to say, 1 at. of ammonio-protochloride of mercury, and 1 at. of basic protochloride of mercury; whilst that produced by ammonia is represented by $HgCl_2 + HgN_2H_4$.—ED.

* Infusion of galls produces no precipitate in solutions of protoxyde of mercury.

Hydrosulphuret of ammonia poured in small quantity in solutions of protoxyde of mercury produces a black precipitate of sulphuret of mercury, which becomes perfectly white when it is shaken with the dissolved salt of protoxyde of mercury, which the re-agent has not been able to decompose; this white precipitate remains a long time suspended in the liquor, and is a combination of sulphuret of mercury, with the salt of protoxyde of mercury contained in the solution. If a fresh quantity of hydrosulphuret of ammonia is gradually added, the precipitate becomes a mixture of black and white. Various mixtures of the combination just mentioned with sulphuret of mercury, produce precipitates which at first may appear brownish-red. When an excess of the re-agent has been employed, the precipitate is completely black, and after the above combination has been entirely decomposed by hydrosulphuret of ammonia, it consists altogether in a sulphuret of mercury, which is quite insoluble in the cold in an excess of hydrosulphuret of ammonia. It is also insoluble in ammonia; but a solution of potash completely dissolves it, provided too little hydrosulphuret of ammonia has not been added in the first instance. It may be precipitated from this alkaline solution by supersaturating it with an acid.

The aqueous solution of sulphuretted hydrogen, or a current of the gas, behaves in the same manner with acid, or with neutral solutions of protoxyde of mercury; the phenomena are, however, more easily observable with sulphuretted hydrogen than with hydrosulphuret of ammonia.

A bar of metallic zinc produces the same effect with solutions of protoxyde as with those of suboxyde of mercury already described.

Solutions of protoxyde of mercury may likewise be recognized by the following re-agents:

A solution of IODIDE OF POTASSIUM produces a red precipitate of a vermillion colour, which is soluble in an excess of the re-agent, and also in an excess of the solution of protoxyde of mercury and in muriatic acid.

A solution of CHROMATE OF POTASH determines a reddish-yellow precipitate of chromate of mercury, in the solutions of protoxyde of mercury which are not too dilute.

Solutions of protoxyde of mercury behave with metallic COPPER in the same manner as solutions of suboxyde of mercury.

The salts of protoxyde of mercury, either soluble or insoluble in water, are volatilised and decomposed when exposed to a red heat.

* Protochloride, protobromide, and proto-iodide of mercury, however, may be sublimed without decomposition.

Neutral solutions of salts of protoxyde of mercury redden litmus paper.

Almost all the salts of mercury insoluble in water are soluble in acids. The best manner to detect the presence of protoxyde of mercury in this acid solution, consists in adding gradually aqueous solution of sulphuretted hydrogen thereto. If there be still some undecomposed protoxyde of mercury in the liquor, a white precipitate is produced by this addition of sulphuretted hydrogen which remains suspended for a long time, and which is converted into a black heavy precipitate by an excess of liquid sulphuretted hydrogen.

* The salts of protoxyde are, like those of suboxyde of mercury, easily reduced before the blow-pipe; after having been mixed with soda, protochloride, proto-iodide, and protobromide of mercury, when mixed with soda, may be partly volatilised without decomposition. When heated, this accident may, however, be easily avoided by very slightly moistening the mixture before submitting it to the action of the heat. When a portion of protoxyde of mercury which has been adulterated with red lead, or with brick-dust, is heated upon charcoal with the blow-pipe, the lead or the brick-dust is left upon the charcoal, by which means the fraud is at once detected.

The salts of protoxyde of mercury may be recognized by their behaviour with hydrosulphuret of ammonia, or still better, this salt being too concentrated, by their behaviour with the solution of sulphuretted hydrogen. In the dry way: the production of globules of mercury is a decisive proof of the existence of that metal.

The presence of such organic substances as cannot be volatilised without undergoing decomposition, has much influence upon the deportment of solutions of protoxyde and of protochloride of mercury with the preceding re-agents, even though these solutions be not coloured by the above said organic substances. If sugar, for example, or non-volatile organic acids be added to a solution of protoxyde of mercury, an excess of solution of potash being subsequently poured therein does not immediately produce any precipitate, if the liquid contains only a small quantity of protoxyde of mercury; but if this solution of protoxyde of mercury be concentrated, a precipitate of a dirty yellow colour is at first formed, but in either case a black heavy sediment is after a time deposited, which contains suboxyde of mercury and much metallic mercury. This black precipitate is immediately determined by boiling. The same phenomena are produced when carbonate of soda or of potash is used instead of pure potash. Were an alkali not added, the reduction into metallic mercury would not take place. Ammonia produces in such solutions of protoxyde of mercury a white precipitate, which keeps its colour for a long time, and which partly turns black by boiling.

* It is often said that the action of organic substances upon protochloride of mercury is to change it into subchloride of mercury and metallic mercury. Supposing this to take place, it is a rare case, for it is only by the addition of a fixed alkali that the reduction of protochloride of mercury into suboxyde of mercury and metallic mercury can take place. It often happens that a solution of protochloride of mercury (sublimate) produces white precipitates in solutions of organic substances, but these precipitates ordinarily consist of a combination of the organic

substance with protoxyde of mercury, and they contain no subchloride of mercury, as is frequently supposed. By the addition of an alkali, on the contrary, they are reduced, especially with the help of heat, into suboxyde of mercury and metallic mercury.

When solutions of protoxyde of mercury are strongly coloured by organic substances, for example, when they contain red wine, solution of potash immediately produces dark-coloured precipitate of various hues, which, by standing, or more rapidly still by boiling, become black, and consist of suboxyde of mercury and metallic mercury. White wine containing much protochloride of mercury (sublimate) in solution is coloured reddish-brown by solution of potash, but no immediate precipitate appears; it is only after a pretty considerable time, or more rapidly by boiling, that at first a dirty reddish-brown and then a grey precipitate is formed.

* When an excess of hydrosulphuret of ammonia or of solution of sulphuretted hydrogen is poured in solutions of protoxyde of mercury, mixed with much organic matter, it sometimes occurs that no black precipitate of sulphuret of mercury is thereby produced. The precipitate is often yellow or brown, according to the nature of the various organic substances, and it is only when ammonia is added that it becomes black; but when a black precipitate of sulphuret of mercury is immediately produced, this precipitate can seldom be distinguished in liquids which are of a very dark colour. In order fully to convince one's self that mercury is present, the precipitated sulphuret must be collected on a filter, dried, mixed with soda, and reduced into metallic mercury by heating it in a small glass tube, closed at one end. But as the sulphuret of mercury may remain suspended for a long time in the liquid when this liquid contains certain organic substances, and as, in such a case, it is difficult, sometimes impossible, to collect it on a filter, sulphuretted hydrogen should be resorted to for precipitating the mercurial solution only when the proportion of mercury is very considerable. The safest method to discover a small quantity

of mercury in such liquids consists in plunging therein a sheet of bright copper. The liquid should be neutral, or at least only slightly acid; but mercury can also be precipitated from an alkaline liquid by copper. It does not matter in such a case whether the liquid is very dark or only slightly coloured, or whether it contains this or that kind of organic matter. However feeble the traces of mercury dissolved therein, the copper, after a time, becomes coated with a grey film, which, upon being rubbed with paper, shows an argentine surface, which a moderate heat soon dissipates. When the quantity of mercury dissolved is extremely minute, the apparent silvering of the copper is very slight; for the ruddy hue of the copper may be seen through. In such a case the original colour of the copper should be reproduced by heating the copper in several places, and then the silvery appearance of the spots which have not been heated becomes more distinct when compared with the other places in which the pure copper colour has been restored.

* According to J. Smithson the following method should be adopted for the purpose of detecting extremely minute traces of persalt of mercury in any kind of liquid. Take a small foil of pure gold, or a strong gold wire, round which a thin strip of tin-foil is to be coiled, and plunge it in the liquid under examination, which liquid should be previously acidulated with a few drops of muriatic acid. After a time (several hours may be required if only a very minute quantity of mercury is in solution) the mercury is precipitated upon the gold, and has silvered it. By heating the gold the mercury is volatilised, which at once identifies the metal, and the gold re-assumes its original colour.

* Although extremely minute quantities of mercury may be detected by this method, yet Orfila is of opinion that it may often be a subject of error. After a time some tin may be dissolved, and reduced so as to whiten the gold, and thus simulate the presence of mercury, which all the while may be absent. When the gold thus whitened is exposed to heat, it may even recover its golden colour. It is therefore better not to expose

it to heat, but to digest it in a little concentrated muriatic acid. If the white colour was owing to the reduction of tin, the tin is dissolved by the acid, and the golden colour re-appears; if, on the contrary, the white colour was caused by mercury, it does not disappear; when such is the case the gold is removed from the acid, and put into a narrow tube, closed at one end, in which it is to be heated: a little mercury is sublimed, and the gold re-assumes its pristine colour.

* This mode of reducing mercury from its solutions may be advantageously resorted to when these solutions contain much organic matter so as to appear very dark.

When protoxyde of mercury is contained in organic substances in the solid or in the pasty state, and which are insoluble in water, it is advisable, in some cases, to try whether they can be dissolved by ammonia. Thus, for example, the solutions of protochloride of mercury (sublimate) form, with solutions of albumen, a precipitate which is insoluble in water, but which is very readily soluble both in ammonia and in solution of potash. Hydrosulphuret of ammonia poured in such an ammoniacal solution precipitates mercury in the state of sulphuret; but this precipitate remains for a long time in suspension, and can scarcely be separated from the solution for the purpose of drying it, and then of submitting it to the action of the blow-pipe, in order to ascertain whether it contains mercury. It is therefore preferable to plunge a strip of bright copper in the ammoniacal solution from which the mercury can thus be precipitated in the metallic state exactly as would be the case with a neutral or slightly acid solution; the mercury thus precipitated by copper forms a superficial coating of a grey colour, which assumes a silvery appearance by friction with a piece of paper. Even exceedingly small traces of mercury can be thus detected in an ammoniacal solution, and perhaps also it is the best test which could be employed for the purpose of ascertaining the presence of mercury in blood with which a certain quantity of this metal might have been mixed, since all the constituent principles of the blood are soluble in excess of ammonia.

It is, however, necessary in such experiments not to employ solution of potash instead of ammonia; for the presence of mercury in a potash solution, even though such a solution be clear, cannot be detected in hydrosulphuret of ammonia, because the sulphuret produced by this re-agent remains dissolved when there is enough potash (page 138). A strip of copper precipitates also mercury from such a solution, but not so well as from an ammoniacal solution.

When the organic matter containing mercury is insoluble both in water and in ammonia, it is customary to digest it with nitric acid; but this method is often a source of inconvenience, especially when the quantity of organic substances is very abundant, and that of the mercury very small. In such cases it is preferable to adopt the following course:—The dry substance is to be mixed with about the third or the fourth of its weight of carbonate of soda or of carbonate of potash, and the mixture is to be introduced in a retort so as to leave the three-fourths of it empty; water is poured in the retort in sufficient quantity so that by shaking the retort the whole of the contents has the consistency of pap or batter. If the substance which contains the mercury is in the pasty state, it is to be mixed with some alkaline carbonate, and dried by a gentle heat, in order to facilitate its introduction into the retort. The neck of the retort is then to be connected with a receiver by means of a perforated cork, which must not fit quite air-tight, and the retort is then to be gradually heated till the bottom becomes red hot. When the mixture under examination is not abundant, so that the experiment can be performed in a small retort, a spirit-lamp with circular wick will give a sufficient heat; but if larger quantities are operated upon, ordinary fuel must be employed. Ordinarily the mixture swells up greatly, and care must in consequence be taken that it should not pass into the neck of the retort. After cooling, the neck of the retort is to be cut immediately near the roof, and the neck thus cut off is again to be split longitudinally, in order to have access to its inner surface, which is found covered with a brown empyreumatic viscid oil. At the distance of about one inch from the roof of the retort small globules of mercury may be found. The best way of ascertaining that they really are globules of mercury consists in rubbing the finger on the spot where the operator thinks he perceives some, and it is then easy to distinguish them on the finger where the matter has adhered, either with the naked eye, or, what is better, with the help of a magnifying glass. This precaution is necessary, because small bubbles of air, inclosed in the empyreumatic oil, simulate minute globules of mercury, and may be mistaken for such by an unexperienced analyst. If the organic matter contained only slight traces of mercury, the whole of the metal is found in the neck of the retort, and none has passed with the empyreumatic oil into the receiver. This method gives more correct results than is generally believed. If no mercury should be found in the neck of the retort, the oil in the receiver and the broken pieces of the neck of the retort, with the oil adhering to them, may be digested in nitric acid, in order to test for mercury the acid solutions thus obtained. If, however, the operation having been conducted with great care, no mercury is found in the neck of the retort, the nitric acid solution will seldom afford a trace of mercury.

* When a dry organic substance is mixed with protochloride of mercury (sublimate) it is often necessary to add water or alcohol, in order to extract the mercurial salt, the presence of the metal can then be easily recognised in the aqueous or alcoholic solution by means of the re-agents above mentioned. Water is employed to dissolve protochloride of mercury (sublimate) when the organic substance is insoluble in that vehicle, and alcohol when the organic substance is not acted upon by spirit. If the organic substance is insoluble both in water and in alcohol, this last menstruum deserves the preference, because protochloride of mercury is more soluble in it than in water.

27. OXYDES OF PLATINUM.

[1°. PROTOXYDE OF PLATINUM, PtO.]

(*Oxyde Platineux.*)

* PROTOXYDE of platinum in the state of hydrate is black. The corresponding protochloride of platinum (*chlorure platineux*) is dark-brown, and is insoluble in water, but soluble in a solution of perchloride of platinum, and in muriatic acid. When heated with aqua regia, it is converted into perchloride of platinum; its muriatic acid solution behaves with re-agents like that of protoxyde of platinum in acid.

* An excess of a solution of POTASH poured in such solutions produces no precipitate. If, however, the liquor contains a little perchloride of platinum, a slight yellow precipitate of potassio-chloride of platinum is produced.

* AMMONIA poured in excess in a solution of protochloride of platinum determines a green crystalline precipitate of ammonio-chloride of platinum, and the supernatant liquid is as limpid as water.

* A solution of CARBONATE OF POTASH produces in solutions of protochloride of platinum a brownish precipitate, which requires some time for settling; the supernatant liquid retains a brownish-red colour, and by long standing it turns black; this change beginning at the surface.

* A solution of CARBONATE OF SODA behaves like one of carbonate of potash.

* A solution of CARBONATE OF AMMONIA produces no precipitate in that of protochloride of platinum.

* A solution of PHOSPHATE OF SODA determines no precipitate either, even after neutralising the free muriatic acid by potash.

* A solution of OXALIC ACID produces no precipitate in solutions of protochloride of platinum.

* A solution of FERROCYANURET OF POTASH, nothing.

* A solution of FERRICYANURET OF POTASH, nothing.

* A solution of PERCHLORIDE OF MERCURY, nothing.

* A solution of NITRATE OF SUBOXYDE OF MERCURY produces a black precipitate.

* A solution of PROTOSULPHATE OF IRON produces no precipitate in that of protochloride of platinum.

* A solution of PROTOCHLORIDE OF TIN imparts a brownish-red colour in that of protochloride of platinum; but no precipitate is produced.

* A solution of IODIDE OF POTASSIUM at first communicates a dark brownish-red colour to solution of protochloride of platinum; but after a time a black precipitate is produced, having a metallic lustre, and the liquor is left colourless.

* Aqueous solution or a current of SULPHURETTED HYDROGEN GAS imparts a brown colour to the neutral, and to the acid solutions of protochloride of platinum. Yet after some time a black precipitate of sulphuret of platinum is formed.

* HYDROSULPHURET OF AMMONIA produces in solution of protochloride of platinum after saturation with potash, a blackish-brown precipitate of sulphuret of platinum soluble in a large excess of the re-agent. The solution has a dark reddish-brown colour.

* Solutions of protochloride of platinum are easily recognized, more especially by the green precipitate produced by ammonia. When heated with aqua regia, the protochloride of platinum becomes converted into perchloride of platinum, which may be easily identified by means of the re-agents mentioned under the next head.

* When non-volatile ORGANIC SUBSTANCES are mixed with solution of protochloride of platinum, solutions of carbonate of potash or of soda poured in it at first produce no change; but after some time the solution assumes a black colour. The development of the characteristic green precipitate produced by ammonia in solution of protochloride of platinum is not impeded by the presence of non-volatile organic substances,

2°. PEROXYDE OF PLATINUM, PtO_2.

[DEUTOXYDE OF PLATINUM.]

(*Oxyde Platinique.*)

It is probable that pure peroxyde of platinum is never met with in the course of analytical researches. Hydrate of deutoxyde of platinum is a reddish-brown powder, which by exposure to heat becomes dark-brown, or almost black, and gives out water. By a stronger heat, hydrated peroxyde of platinum disengages oxygen, and metallic platinum is reduced.

* Its combination with acids forms red or yellow salts; but it has also a rather strong affinity for basic substances, and it combines with the alkalies.

The corresponding perchloride of platinum forms a dark brownish-red saline mass, which becomes converted into protochloride of platinum when heated almost to the temperature of melting lead[1], and into metallic platinum by a further increase of temperature. In both cases chlorine gas is disengaged when perchloride of platinum is heated less strongly than is requisite to convert it entirely into protochloride of platinum; it is completely soluble in water, to which it communicates a brown colour of so deep a hue that the solution appears opaque. This liquid consists of protochloride dissolved in perchloride of platinum.

Perchloride of platinum is soluble in water and in alcohol; the solution has a deep brown colour, and resembles much that of neutral perchloride of iron.

* This solution has still an intense colour when it is so dilute as not to afford any precipitate with solution of chloride of potassium.

The aqueous solution behaves towards re-agents like that of platinum in aqua regia, which contains perchloride of platinum.

A solution of POTASH produces a yellow precipitate of potassio-chloride of platinum, especially when a little muriatic acid is added, in order to convert the potash into chloride of potassium[1]. The precipitate is not sensibly soluble in free acids, but it is soluble, with the help of heat, in an excess of potash, and does not separate from the liquor on cooling. It re-appears in such a liquor by supersaturating it with muriatic acid. * A very large quantity of water is required to dissolve it.

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[1] Lead melts at about 612° Fahr.—Ed.

AMMONIA produces in solutions of perchloride of platinum, (especially if a little muriatic acid be added to convert the ammonia into muriate of ammonia) a yellow precipitate similar to that produced by solutions of potash, and which is insoluble in free acids.

* This precipitate is a combination of the two salts forming an ammonio-chloride of platinum soluble in a very large quantity of water.

It is also soluble with the help of heat in excess of ammonia, and if such a solution be supersaturated by muriatic acid, a white precipitate is thrown down.

A solution of CARBONATE OF POTASH produces in solutions of persalts of platinum, especially by adding a little muriatic acid, in order to convert the potash into chloride of potassium, a yellow precipitate of potassio-chloride of platinum insoluble in an excess of the re-agent, even with the help of heat.

A solution of BICARBONATE OF POTASH behaves in the same manner.

A solution of CARBONATE OF SODA does not produce, in the cold, any precipitate in solutions of perchloride of platinum, even when left for a long time in contact.

* If, however, the mixture be kept boiling for a long time, a brownish-yellow precipitate of platinate of soda is produced.

A solution of CARBONATE OF AMMONIA behaves like that of carbonate of potash; the yellow precipitate which is formed is an ammonio-chloride of platinum.

A solution of PHOSPHATE OF SODA produces no precipitate.

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[1] Without this precaution the free alkali might prevent the precipitation of the double chloride.—ED.

A solution of OXALIC ACID produces no precipitate.

A solution of FERROCYANURET OF POTASSIUM produces a precipitate of potassio-chloride of platinum, and the liquor assumes a slightly darker colour.

A solution of FERRICYANURET OF POTASSIUM behaves like the preceding re-agent.

A solution of CYANURET OF MERCURY produces no precipitate.

A solution of SUBNITRATE OF MERCURY determines an abundant reddish-yellow precipitate.

A solution of PROTOSULPHATE OF IRON produces no precipitate.

PROTOCHLORIDE OF TIN imparts a dark reddish-brown colour to solutions of perchloride of platinum[1], without producing a precipitate.

A solution of IODIDE OF POTASSIUM likewise communicates a dark reddish-brown colour to solutions of perchloride of platinum; but it determines besides a brown precipitate of a lighter hue. When the liquor is heated, the glass becomes covered with a metallic coating.

* INFUSION OF GALLS produces no precipitate.

Aqueous solution, or a current of SULPHURETTED HYDROGEN GAS poured in neutral, or in acid solutions of perchloride of platinum first renders them brown only; but after a time a brown precipitate of bisulphuret of platinum is formed, which, after settling at the bottom of the vessel, appears black[2].

HYDROSULPHURET OF AMMONIA produces in solutions of perchloride of platinum a blackish-brown precipitate of bisulphuret of platinum soluble in a pretty large excess of the re-agent. The solution has a deep reddish-brown colour.

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[1] This colour is due to the reduction of the perchloride of platinum to the state of protochloride.—ED.

[2] When the liquor is heated, solution of sulphuretted hydrogen forms an immediate precipitate of bisulphuret of platinum, soluble, according to Dr. Fresenius, in a very large excess of the re-agent, or of alkaline sulphuret, and readily in aqua regia, but insoluble in muriatic and in nitric acids. Berzelius says, however, that bisulphuret of platinum is soluble, with the help of heat, in concentrated nitric acid, by which it is converted into persulphate of platinum.—ED.

A bar of metallic zinc precipitates platinum in the metallic state from its solutions, under the form of a black powder.

The combinations of peroxyde, and of perchloride of platinum, are decomposed when exposed to a red heat; metallic platinum is left whilst the acid, if volatile, as well as the oxygen, or the chlorine, escape in the gaseous state. If the combinations of perchloride of platinum contain a metallic chloride, which is neither volatile nor decomposable by heat, this metallic chloride, after calcining, remains mixed with minutely divided platinum.

Solutions of the compounds of peroxyde of platinum, and that of perchloride of platinum, redden litmus paper; * but the compounds which perchloride of platinum forms with other chlorides do not alter the colour of blue litmus paper.

* In order to ascertain the presence of platinum in the compounds of that metal which are insoluble in water, the peroxyde or the perchloride of platinum must be reduced into metallic platinum by ignition. The metallic platinum is then to be dissolved in aqua regia, and by means of the above-mentioned re-agents, platinum may easily be detected in the solution.

Before the BLOW-PIPE, compounds of platinum are easily reduced, and communicate no colour to the flux.

Compounds of peroxyde and of perchloride of platinum are very easily recognized in their solutions, and distinguished from every other substance, by their behaviour towards potash and ammonia. When the solution of platinum in aqua regia is very acid, it is sufficient to add some pure potash, or carbonate of potash, or ammonia, to produce the characteristic yellow precipitate; when the solution is neutral, a concentrated solution of chloride of potassium, or of muriate of ammonia, should be poured in it, or else the liquor may be rendered slightly acid by addition of muriatic acid.

The presence of non-volatile organic substances, provided they be not too abundant, in the solution of platinum, does not hinder the formation of the yellow precipitate by potash; but if the quantity of organic matter is too large, the liquor in which potash has been poured becomes quite black by long standing, and then the production of the potassio-chloride of platinum is difficult to see. When the solution of a compound of perchloride of platinum, containing alcohol, has been exposed to a prolonged digestion at a gentle heat, so as to evaporate nearly all the alcohol, the aqueous liquor which then remains yields, by adding solution of cyanuret of mercury, a bulky white precipitate, if not immediately, at least after a time, and by long standing this precipitate becomes still more abundant. Considering that solutions of platinum which contain no organic matter yield no precipitate by CYANURET OF MERCURY, platinum might be confounded with palladium. But if, after having dried the precipitate, it be ignited, it becomes converted into metallic platinum, which, being dissolved in aqua regia, may be easily detected as such by means of the re-agents.

* When platinum is precipitated in an extremely divided state from solutions which contain organic substances, it forms the substance known as ethiops, or platinum black, which is identified by the property which it possesses, of rapidly converting alcohol into acetic acid, in contact with the air.

28. OXYDES OF PALLADIUM.

[1°. PROTOXYDE OF PALLADIUM, PdO.]

(*Oxyde Palladeux.*)

* HYDRATE of protoxyde of palladium is dark-brown; when heated it loses its water, and becomes black. A solution of protoxyde of palladium is produced when palladium is treated by nitric acid, in which, however, it is rather difficultly soluble. The corresponding protochloride of palladium is formed when the metal is treated by aqua regia, in which it may be pretty easily dissolved. The solution has a reddish-brown colour, and in this respect resembles that of perchloride of platinum, but is much darker. Solution of protochloride of palladium, when free from bichloride of palladium, behaves towards some re-agents in a different manner from that of palladium in nitric acid.

* A solution of POTASH produces in the solutions of protoxyde,

and of protochloride of palladium, an abundant brownish-yellow precipitate, which is a subsalt, soluble in an excess of alkali.

* AMMONIA produces no precipitate in solution of nitrate of protoxyde of palladium, but an excess of that alkali renders it colourless. In solutions of protochloride of palladium ammonia determines an abundant flesh-coloured precipitate, which is an ammonio-chloride of palladium, insoluble in a large excess of the precipitant, at least immediately; for by long standing the mixture completely dissolves, and becomes colourless; if it retains a bluish tinge, it is generally a proof that the solution of protochloride of palladium contained protoxyde of copper.

* A solution of CARBONATE OF POTASH produces in solutions of protosalts of palladium a brown precipitate of hydrated protoxyde of palladium, soluble in an excess of the re-agent; but if the whole be boiled, the liquor first assumes a dark colour, and then deposits a brown precipitate[1].

* A solution of BICARBONATE OF POTASH produces in solutions of protosalts of palladium a brown precipitate, soluble in an excess of the re-agent.

* A solution of CARBONATE OF SODA produces in solutions of protosalts of palladium a brown precipitate of protoxyde of palladium, slightly soluble in an excess of the re-agent. If muriatic acid be added to dissolve the precipitate, an excess of solution of carbonate of soda poured in the liquor gives no precipitate; but if the whole be boiled the liquor at first assumes a dark tinge, and then deposits a brown precipitate.

* A solution of CARBONATE OF AMMONIA behaves like ammonia.

* A solution of PHOSPHATE OF SODA creates a brown precipitate in solutions of protosalts of palladium.

* A solution of OXALIC ACID does not produce any precipitate in solutions of protosalts of palladium, provided they be as neutral as possible. The solution of a neutral alkaline oxalate produces

a brownish-yellow precipitate in neutral solutions of protosalts of palladium.

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[1] Berzelius says that the precipitation by carbonate of potash or soda, is accompanied with a disengagement of carbonic acid.—ED.

* A solution of FERROCYANURET OF POTASSIUM at first produces no change in solutions of protosalts of palladium, but after a time a thick and firm jelly is determined.

* A solution of FERRICYANURET OF POTASSIUM does not produce any immediate precipitate, but after a time it also forms a jelly.

* A solution of CYANURET OF MERCURY produces, in solutions of protosalts of palladium, a gelatinous yellowish-white precipitate, which, by standing, becomes almost completely white. This precipitate is soluble in an excess of muriatic acid. When the solution of protosalts of palladium is slightly acid, the precipitate which cyanuret of mercury forms does not appear, except after a long time.

* A solution of SUBNITRATE OF MERCURY does not produce any precipitate in solutions of protoxyde of palladium; but it yields an abundant black precipitate in those of protochloride of palladium.

* A solution of PROTOSULPHATE OF IRON produces no precipitate in somewhat diluted solutions of protosalts of palladium; but it determines a slight precipitate of a black colour when these solutions are concentrated.

* PROTOCHLORIDE OF TIN forms a black metallic precipitate in solutions of protosalts of palladium, and the supernatant liquid has a beautiful dark-green colour.

* A solution of IODIDE OF POTASSIUM produces a black precipitate in solutions of protosalts of palladium, and the liquor becomes dark.

* Aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, produces a black precipitate of sulphuret of palladium in neutral or acid solutions of protosalts of palladium.

* HYDROSULPHURET OF AMMONIA produces also a black precipitate of sulphuret of palladium, insoluble in an excess of the re-agent.

* A bar of METALLIC ZINC precipitates metallic palladium from its solutions under the form of a black powder.

* Most of the compounds of palladium, like those of platinum, are decomposed by exposure to a red heat.

* And as the compounds of palladium, which are insoluble in water, undergo the same sort of decomposition, the presence of palladium may be easily detected by dissolving in aqua regia the metal which has been reduced by ignition, and then testing the solution with the proper re-agents.

* The best method to recognize the presence of palladium in solutions consists in its behaviour towards CYANURET OF MERCURY, which re-agent more especially distinguishes it from solution of perchloride of platinum, with which it might be confounded on account of the colour of the solution. It is, however, necessary to observe that, in some cases, solution of perchloride of platinum may also be precipitated by cyanuret of mercury (page 152); but after all it is easy to separate palladium in the metallic state from its compounds, and then it may be very easily distinguished from the other metals which resemble it by the methods, of which we will speak further on.

* The presence of non-volatile ORGANIC SUBSTANCES prevents potash from precipitating protoxyde of palladium from its solutions; but does not influence the action of cyanuret of mercury [1].

2°. PEROXYDE OF PALLADIUM, PdO_2.

[DEUTOXYDE OF PALLADIUM.]

(*Oxyde Palladique.*)

* BERZELIUS was the first who experimentally demonstrated the existence of this oxyde. The corresponding perchloride of palladium is contained in small quantity in the aqua regia solutions of palladium, but when these solutions are heated for a long time, all trace of it commonly disappears. With chloride of potassium, and with muriate of ammonia, it forms compounds which, like the corresponding solutions of perchloride of platinum, are very sparingly soluble in water and in alcohol, and have a

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[1] The neutral solutions of nitrate of protoxyde of palladium are precipitated yellow by neutral phosphates, arseniates, oxalates, tartrates, and citrates.—ED.

cinnabar or brownish-red colour. Solution of perchloride of palladium is dark-brown. When this solution is heated, chlorine is disengaged, and protochloride of palladium is formed. This characteristic test may easily be resorted to for the purpose of distinguishing it from perchloride of platinum, and from perchloride of iridium, which it resembles in point of colour.

29. OXYDES OF RHODIUM.

1°. PROTOXYDE OF RHODIUM, RO.

(*Oxyde Rhodeux.*)

* PURE protoxyde and protochloride of rhodium are as yet almost unknown. Berzelius has found them combined with peroxyde and perchloride of rhodium.

2°. PEROXYDE OF RHODIUM, R_2O_3.

[SESQUIOXYDE OF RHODIUM.]

(*Oxyde Rhodique.*)

* PEROXYDE of rhodium is black. Hydrate of peroxyde of rhodium obstinately retains its water, or parts with it only by a prolonged ignition; it has then a greyish-green colour. Peroxyde of rhodium is formed when rhodium mixed with platinum is dissolved in aqua regia, rhodium alone being insoluble in that re-agent. It is likewise formed when finely divided rhodium is mixed with potash and a little nitre, and the mixture subjected to an incipient red heat. Lastly, peroxyde of rhodium is always produced by a prolonged ignition of rhodium in contact with the air. In such a case, however, it contains some protoxyde of rhodium. Peroxyde of rhodium is reduced into metallic rhodium, when it is heated with substances which contain charcoal, or when treated by hydrogen gas. Ignition renders it insoluble in acids; its solubility, however, may be restored by fusing it with bisulphate of potash in a platinum crucible, and treating the fused mass by water. This fused mass has a reddish colour, but when quite cold, it appears yellow. The solution is yellow. Rhodium may also be dissolved

in the same way[1]. Fischer asserts that it may likewise be dissolved by fusion with superphosphates, or with phosphoric acid.

* Perchloride of rhodium form scompounds of a pink colour[2], with alkaline chlorides. These compounds are insoluble in water, and their solutions are pink. When hydrated peroxyde of rhodium is dissolved in muriatic acid, the solution has a yellow colour, and becomes red only by boiling or evaporation to dryness. The sulphuric acid solution of hydrate of peroxyde of rhodium is likewise yellow, but by adding some muriatic acid to it, and evaporating the whole, the liquor becomes redder, and its solution in water gives a liquid which is pink, and is not rendered yellow by the further addition of any quantity of water whatever.

* Solutions of salts of peroxyde of rhodium, or of the combinations of perchloride of rhodium, behave as follows towards re-agents :—

* A solution of POTASH produces no precipitate, but by boiling a yellowish-brown jelly is formed, which is hydrate of peroxyde of rhodium.

* AMMONIA determines, after a time, an abundant yellowish precipitate of rhodate of ammonia, completely soluble in dilute muriatic acid. Such a solution has a yellow colour.

* A solution of CARBONATE OF POTASH at first does not form any precipitate, but after a time, a yellowish one is produced, which is hydrate of peroxyde of rhodium.

* A solution of CARBONATE OF SODA behaves in the same manner.

* A solution of CARBONATE OF AMMONIA produces no immediate precipitate, but after a very long time, a yellowish precipitate of rhodate of ammonia is formed.

* A solution of PHOSPHATE OF SODA does not form any precipitate in solution of peroxyde of rhodium.

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[1] According to Berzelius, metallic rhodium may be dissolved by fusion in bisulphate of potash, and sulphurous acid gas is disengaged during the reaction.—ED.

[2] The metal received its name in allusion to the pink colour of this perchloride (*ῥόδον, a rose.*)—ED.

* A solution of OXALIC ACID produces no precipitate.

* A solution of FERROCYANURET OF POTASSIUM, nothing.

* A solution of FERRICYANURET OF POTASSIUM, nothing.

* A solution of PROTOSULPHATE OF IRON, nothing.

* A solution of PROTOCHLORIDE OF TIN renders the red solution of peroxyde of rhodium of a dark-brown colour, but no precipitate is formed.

* A solution of IODIDE OF POTASSIUM produces a very dark colour, and ultimately produces a slight precipitate.

* An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, produces no immediate precipitate, but in time a brown precipitate of sulphuret of rhodium takes place, though the supernatant liquor is not discoloured[1].

* HYDROSULPHURET OF AMMONIA produces a brown precipitate of sulphuret of rhodium, insoluble in an excess of the re-agent.

* A bar of METALLIC ZINC precipitates rhodium from its solution in the metallic state, and under the form of a black powder which enfilms the zinc.

* Solutions of peroxyde of rhodium are recognized by the pink colour which they acquire, when after addition of muriatic acid they are evaporated to dryness, and the residuum dissolved in water. Their behaviour towards alkalies, especially towards ammonia, distinguishes solutions of peroxyde of rhodium from those of platinum and of other substances. In the solid state, rhodium may be easily detected in its compounds, by the property which they possess of becoming reduced into metallic rhodium when heated in an atmosphere of hydrogen gas. The rhodium thus reduced is insoluble in aqua regia, but soluble by fusion in bicarbonate of potash; wherefore if a little of the reduced rhodium be mixed with some bicarbonate of potash, and if the mixture be then introduced in a strong glass tube, closed at one end, and heated upon a spirit lamp with a circular wick, the presence of rhodium may be rendered manifest by the colour of

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[1] By heating the solution of salts of rhodium in conjunction with liquid sulphuretted hydrogen, an immediate blackish-brown precipitate is determined.—ED.

the fused mass, which, after cooling, is yellow. Amongst the metals called noble, palladium and silver are the only ones besides rhodium, which are dissolved by fusion with bicarbonate of potash, but rhodium can hardly be confounded with them.

30. OXYDES OF IRIDIUM.

1°. PROTOXYDE OF IRIDIUM, IrO.

(*Oxyde Irideux.*)

* **Protoxyde** of iridium is black; when it has been prepared in the dry way, acids have scarcely any action upon it. Hydrate of protoxyde of iridium is greyish-green, soluble in acids, to which it communicates a green colour. Protochloride of iridium is almost insoluble in water, in acids, and even in aqua regia; it is decomposed by exposure to a dark red heat.

2°. SESQUIOXYDE OF IRIDIUM, Ir_2O_3.

(*Oxyde Susirideux.*)

* **Sesquioxyde** of iridium is a fine black powder, and it is this oxyde which is generally formed both in the dry and in the humid way. It is insoluble in acids, even after having been fused with bisulphate of potash. It is obtained by mixing potassio-chloride of iridium with carbonate of potash or of soda, and exposing the mixture to a slight red heat, lixiviating the saline mass with water, during which operation it does not dissolve, but is easily washed away through the filter, and thus forms a turbid liquid of a bluish-green colour, which deposits the sesquioxyde of iridium when solution of common salt is poured in it. Sesquioxyde of iridium is also produced when iridium is heated with pure potash and nitrate of potash, though the presence of nitre is useless when the operation is performed in contact with the air. The fused compound dissolves partly in water, to which it communicates a deep yellowish-brown colour. This solution, however, is easily decomposed, especially when very dilute. Sesquioxyde of iridium is reduced by a strong white heat, but the reduction may be effected even at the

ordinary temperature by a current of hydrogen gas[1]. A dark red heat is not sufficient to decompose it. Mixed and heated with combustible substances, it is decomposed with a smart detonation. This oxyde appears to be the highest degree of oxydisation of iridium, which may be obtained in the dry way.

The corresponding sesquichloride of iridium is of difficult formation, on account of the insolubility of sesquioxyde of iridium in muriatic acid. The sesquioxide of iridium produced by fusion with nitre, is soluble in muriatic acid, after digestion of the fused mass in nitric acid: the solution has a very dark brown colour.

3°. DEUTOXYDE OF IRIDIUM, IrO_2.

(Oxyde Iridique.)

* THE deutoxyde of iridium and the bichloride of iridium are the most important combinations of all the oxydes and chlorides of that metal. Deutoxyde of iridium could not, however, as yet be isolated, because it is very soluble in alkalies, which consequently cannot precipitate it from its solutions. Deutochloride of iridium is produced when iridium combined with platinum is heated in aqua regia; the acid, however, dissolves only a small quantity of iridium, which alone is insoluble in that acid. The easiest method of obtaining compounds of deutochloride of iridium with other metallic chlorides consists, according to Berzelius, in mixing the metallic chloride with very finely divided iridium, and exposing the mixture in an incipient red heat to the action of a current of chlorine gas.

* Solutions of deutochloride of iridium, and of its combinations with other metallic chlorides, even when very dilute, have a very deep red colour, with a tint of brown. When the liquor is concentrated it appears almost entirely opaque.

* Most of the combinations of deutochloride of iridium with

other metallic chlorides are very sparingly soluble in water. Such are, for example, those which it forms with chloride of potassium or muriate of ammonia. Still, they are more soluble than the corresponding combinations of perchloride of platinum, and they behave as follows towards re-agents.

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[1] This reduction of sesquioxyde of iridium by hydrogen gas at the ordinary temperature, appears to be owing to the property of effecting the combination of the hydrogen with the oxygen of the air, during which reaction it becomes hot enough to be reduced by the hydrogen. This action is similar to that of spongy platinum.—ED.

* An excess of solution of POTASH either immediately discolours them, or converts the dark colour of their solution into a slightly greenish colour, during which change only a very slight trace of a brownish-black precipitate is produced. When such a clear solution is heated, a very trifling change only is at first ordinarily perceivable, but if it be left at rest after having been thus heated, it begins to assume a blue colour. This blue colour, which is owing to a combination of the two oxydes of iridium, gradually becomes more intense from the surface, where it is in contact with the atmosphere, downwards. It somewhat resembles that of a solution of protoxyde of copper in ammonia; yet it has a slight tinge of purple, which is better observed before the liquor has become too dark. If the blue solution be evaporated, a small quantity of blue precipitate is separated; but the dry mass is white, with a greenish tinge. When treated by water, there remains a blue powder, and the supernatant liquid is colourless.

* An excess of AMMONIA poured in these solutions likewise discolours them immediately, absolutely as solution of potash, and produces but a trace of a brownish-black precipitate. By a prolonged boiling, so as almost entirely to dissipate the excess of ammonia, the solution begins to assume a blue colour, but which is not so pure as that produced by potash in deutochloride of iridium. The colouring is, however, more successfully produced by exposing the clear ammoniacal solution to the atmosphere in a shallow vessel. In proportion as the excess of ammonia evaporates, a blue precipitate gradually appears, and the blue colour is at the same time developed.

* A solution of CARBONATE OF POTASH produces at first, in solutions of the combinations of deutochloride of iridium, an abundant precipitate of a brownish-red colour, which is

gradually and spontaneously dissolved, the liquor at the same time becoming colourless, exactly as is the case with pure potash or ammonia, and only a trace of a blackish-brown precipitate likewise remains. If the clear solution be boiled, it does not thereby assume a blue colour. When evaporated to dryness, the residuum, being treated by water, leaves a small quantity of a blue powder, and after a time the liquor becomes blue.

* A solution of BICARBONATE OF POTASH does not at first determine any change in solutions of the compounds of deutochloride of iridium, but after a time they become discoloured, as when they are treated by potash or ammonia, but they yield no precipitate.

* A solution of CARBONATE OF SODA discolours them as solutions of potash and ammonia do. When boiled, the liquid does not at first turn blue, but after a time it takes a blue tinge.

* A solution of CARBONATE OF AMMONIA does not at first produce any change in solutions of compounds of deutochloride of iridium, but after a time it discolours them.

* A solution of PHOSPHATE OF SODA at first does not cause any change, but in course of time these solutions become discoloured or assume a slightly-greenish tinge.

* A solution of OXALIC ACID does not produce any alteration in the first moment, but after a time the solutions become completely discoloured.

* A solution of FERROCYANURET OF POTASSIUM immediately discolours the solutions of the compounds of deutochloride of iridium.

* A solution of FERRICYANURET OF POTASSIUM produces no alteration, even after a long time.

* A solution of CYANURET OF MERCURY, nothing.

* A solution of SUBNITRATE OF MERCURY gives a light-brownish precipitate.

* A solution of PROTOSULPHATE OF IRON discolours the solutions of the compounds of deutochloride of iridium, but produces no precipitate. Yet after a pretty long time a dingy greenish precipitate is formed.

* PROTOCHLORIDE OF TIN produces a light-brownish precipitate.

* A solution of IODIDE OF POTASSIUM from the first discolours the solutions of the compounds of deutochloride of iridium, but produces no precipitate.

* An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, at once discolours the neutral and the acid solutions of the combinations of deutochloride of iridium; after a time, a brown precipitate of sulphuret of iridium is formed.

* HYDROSULPHURET OF AMMONIA produces in the solutions of the compounds of deutochloride of iridium a brown precipitate of sulphuret of iridium, completely soluble in an excess of the re-agent. When such a solution is decomposed by muriatic acid, brown sulphuret of iridium is deposited.

* A bar of METALLIC ZINC plunged in a solution of deutochloride of iridium precipitates, though incompletely, iridium in the metallic state under the form of a black powder.

* The compounds of deutoxyde and of deutochloride of iridium are decomposed by exposure to a red heat.

4°. PEROXYDE OF IRIDIUM, $Ir\,O_3$.

(*Oxyde Suiridique.*)

* HYDRATED peroxyde of iridium is brownish when dissolved in muriatic acid; the liquid is yellow, but becomes red when it is evaporated. Perchloride of iridium has so much resemblance with perchloride of rhodium, that Berzelius thinks that a chemist might be excused for confounding the one with the other.

* The solutions of iridium, which ordinarily contain deutoxyde or deutochloride of iridium, and the colour of which solutions is, in such cases, of a dark brownish-red rarely green, when they contain protochloride of iridium, cannot be confounded with any of the substances which have been hitherto treated of, reference being had to their behaviour towards the alkalies, more especially with solution of potash, and also on

account of the facility with which the combinations of iridium are decomposed by hydrogen gas, and lastly, by reason of the insolubility of metallic iridium in aqua regia. They may be distinguished from the solutions of peroxyde of rhodium, which resemble much those of peroxyde of iridium, by evaporating to dryness and reducing the dry mass by a current of hydrogen gas, and fusing the metal thus obtained with bisulphate of potash. Thus treated, iridium passes into the state of sesquioxyde of iridium, which, however, does not dissolve in the salt, and communicates no colour to it, whilst rhodium does. The reduced metal may also be mixed with chloride of potassium, and the mixture treated in a current of gaseous chlorine, by which means, if any iridium be present, potassio-chloride of iridium is obtained, which has a blackish-brown colour, which in powder is reddish-brown, whilst potassio-chloride of rhodium has a pink colour.

31. OXYDES OF OSMIUM.

1°. PROTOXYDE OF OSMIUM, OsO.

(*Oxyde Osmieux.*)

* PROTOXYDE of osmium has much resemblance with protoxyde of iridium, but most materially differs from it in this, that when heated in contact with the air, it produces peroxyde of osmium (osmic acid), which is volatile, and has an extremely disagreeable odour[1], and which powerfully attacks the eyes and nose. When heated in close vessels, no peroxyde of osmium is formed[2]. Berzelius is the only chemist who has as yet separated protoxyde of osmium. The corresponding protochloride of osmium is green, and can be sublimed[3]. It is soluble in water, but is

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[1] The odour has by some been compared to that of chlorine and of chloride of sulphur, and provokes coughing.—ED.

[2] Heated in close vessels, hydrated protoxyde of osmium gives off water, but does not sublime, nor does it disengage oxygen. Heated with combustible bodies, it detonates, and there is reduction of osmium. Hydrogen gas reduces it at the ordinary temperature, water is formed and heat evolved.—ED.

[3] The colour of the solution of protochloride of osmium is, according to Berzelius, of a remarkably fine green, but only in very concentrated solutions, for when a larger quantity of water is added than is necessary to keep the chloride in solution, the liquor becomes turbid, and there is reduction of osmium. A large

thereby decomposed, the result being peroxyde of osmium, which the water dissolves, and metallic osmium, which is deposited, whilst at the same time muriatic acid is set free. Protochloride of osmium enters into combination with other metallic chlorides.

2°. SESQUIOXYDE OF OSMIUM, Os_2O_3.

(*Oxyde Susosmieux.*)

* **Sesquioxyde of osmium** is formed by dissolving peroxyde of osmium in ammonia. The product of the reaction is a dark brown compound of sesquioxyde of osmium and ammonia [and of water[1]], which, when boiled with solution of potash, and subsequently washed, detonates strongly. Sesquioxyde of osmium is soluble in muriatic acid, and the solution bears some resemblance with solutions of sesquioxyde of iridium in acids.

3°. DEUTOXYDE OF OSMIUM, OsO_2.

(*Oxyde Osmique.*)

* **Deutoxyde of osmium** is black. The corresponding deutochloride of osmium is obtained by mixing metallic osmium with chloride of potassium, and heating the mixture in chlorine gas to incipient redness. The combination has a red colour; the solution is yellow. When such a solution is boiled with sulphuric acid, the disagreeable odour of peroxyde of osmium is evolved.

* The solution of pure deutochloride of osmium, that is, unmixed with chloride of potassium or other metallic chlorides, is

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quantity of water at once discolours the solution, and the reduced osmium is deposited.—Ed.

[1] Berzelius says that the liquor obtained by supersaturating peroxyde of osmium with ammonia is of a golden yellow colour: by exposing it to a temperature of from + 40° to + 60° centigrade nitrogen gas is evolved, the liquor becomes blackish-brown, and a portion of sesquioxyde of osmium is deposited, but the greatest part of it remains dissolved in the ammonia, and is precipitated only during the evaporation. The oxyde thus obtained is black, and after dessication, blackish-brown. It is a combination of sesquioxyde of osmium, ammonia, and water. If heated, it fuses with emission of light, nitrogen is disengaged, and water formed. The metal is, at the same time, reduced, but a great quantity of it is carried away along with the gas. By boiling the above precipitate with potash, it may be obtained in a fulminating state. It is slightly soluble in acids, and these solutions are yellowish-brown, becoming altogether black. The acid solutions of this oxyde are not precipitated by either iron or zinc.—Ed.

very rapidly decomposed into peroxyde of osmium, metallic osmium, and muriatic acid. The combinations of this chloride with other metallic chlorides, however, do not undergo any decomposition when dissolved in water.

* A solution of POTASH does not produce any change at first in solutions of combinations of deutochloride of osmium, but by heating the liquid it assumes a black colour caused by deutoxyde of osmium, a black precipitate is deposited, and the liquid becomes clear again. By leaving the mixture undisturbed for a long time, the same effect is produced as by boiling.

* AMMONIA does not cause at first any change in solutions of potassio-chloride of osmium, but after a time the liquor becomes brown, and a precipitate of the same colour is deposited.

* CARBONATE OF POTASH at the beginning produces no change in solution of potassio-chloride of osmium, but after a time a black precipitate of deutoxyde of osmium is formed, and the supernatant liquid is bluish.

* A solution of BICARBONATE OF POTASH behaves in the same manner, only the liquor must be boiled to determine the formation of the black precipitate.

* A solution of CARBONATE OF SODA behaves like a solution of carbonate of potash, with only this difference: that the supernatant liquor above the black precipitate has a less dark blue colour.

* A solution of CARBONATE OF AMMONIA behaves like ammonia towards solutions of deutochloride of osmium.

* A solution of PHOSPHATE OF SODA at first does not produce any change in solutions of deutochloride of osmium; but after a time a black precipitate is produced, and the supernatant liquor is bluish.

* A solution of OXALIC ACID causes no alteration in solution of potassio-chloride of osmium, even after a pretty long time.

* A solution of FERROCYANURET OF POTASSIUM behaves in the same manner.

* A solution of FERRICYANURET OF POTASSIUM, the same.

* A solution of CYANURET OF MERCURY, the same.

* A solution of subnitrate of mercury produces a yellowish-white precipitate in solution of potassio-chloride of osmium.

* A solution of protosulphate of iron produces no change.

* Protochloride of tin gives a brownish precipitate.

* A solution of iodide of potassium at first does not cause any alteration in solution of potassio-chloride of osmium; but by long standing a black precipitate is formed, and the liquor becomes bluish.

* Aqueous solution, or a current of sulphuretted hydrogen gas, does not at first cause any alteration in solution of potassio-chloride of osmium; but after a time a brownish-yellow precipitate of sulphuret of osmium is produced.

* Hydrosulphuret of ammonia produces a brownish-yellow precipitate of sulphuret of osmium insoluble in an excess of the re-agent.

* A bar of metallic zinc plunged in solutions of osmium precipitates this metal in the form of a black powder, though incompletely.

4°. PEROXYDE OF OSMIUM, OsO_3.

(Oxyde Susosmique—Acide Osmique.)

* This oxyde is formed when metallic osmium or its other oxydes are heated in contact with the air, and also when the solutions of osmium are boiled in nitric acid. Peroxyde of osmium is well distinguished by its volatility, and the extremely disagreeable odour of its vapours[1]. It possesses so many of the properties which distinguish acids, that we shall defer speaking of it until we come to the chapter which treats of acids[2].

* The compounds of osmium may very easily be recognized, because when their solutions are boiled with an excess of nitric acid, the disagreeable odour of peroxyde of osmium is evolved; and because they may be reduced by a current of hydrogen gas

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[1] It is from the odour of this oxyde that the name of the metal has been taken; ὀσμῆ, odour.—Ed.

[2] Peroxyde of osmium has no acid reaction, but it unites with alkalies, forming with them compounds which are permanent at high temperatures.—Ed.

into metallic osmium, which, like the oxydes of osmium, exhale that characteristic odour when heated in contact with the air. When, however, compounds of osmium contain iridium, they resist much more powerfully the action of nitric acid, and of oxygen. It is better in such a case to reduce them by means of hydrogen gas[1], since, when in the metallic state, the minutest trace of osmium can be detected in iridium by means which will be exposed further on.

32. OXYDES OF GOLD.

1°. SUBOXYDE OF GOLD, Au_2O.

(*Oxyde Aureux.*)

Suboxyde of gold is obtained from subchloride of gold by means of a solution of potash; but its existence is but of short duration, for it soon becomes converted into metallic gold and peroxyde of gold. In the same way, subchloride of gold is decomposed into metallic gold and perchloride of that metal[2].

2°. PEROXYDE OF GOLD, Au_2O_3.

[SESQUIOXYDE OF GOLD.]

(*Oxyde Aurique.*)

Hydrate of peroxyde of gold is brownish-yellow. When peroxyde of gold has been precipitated from solutions of perchloride of gold by a base, it always retains a certain quantity of that base.

* It combines in general with the bases, with which it plays

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[1] Peroxyde of osmium is not reduced by hydrogen gas at the ordinary temperature into the inferior degrees of oxydisation of this metal: the help of heat is required. Berzelius gives the following directions:—Expose the peroxyde of osmium to a gentle heat, and cause a current of hydrogen gas to enter the vessel in which the peroxyde is contained, and the gaseous mixture so produced to pass through a glass tube, part of which is made red hot. Water is formed, and metallic osmium is gradually deposited in the state of a cohesive mass on or about the part where the glass is red hot.—Ed.

[2] Subchloride of gold is permanent when dry, but the contact of water gradually decomposes it into perchloride and metallic gold. This decomposition is instantaneous when boiling water is poured upon it: two parts of metallic gold are precipitated for one which remains in solution.—Ed.

the part of an acid. It is insoluble, or almost so, in the oxacids: concentrated sulphuric acid, and concentrated nitric acid, each dissolve it; but the affinity is so feeble, that the addition of water to the solution is sufficient to precipitate it. Exposed to a red heat, it is converted into metallic gold, and oxygen gas is evolved.

The corresponding perchloride of gold is contained in the solution of gold in aqua regia. Heated to the temperature at which tin melts, it is converted into subchloride of gold; a stronger heat reduces it into metallic gold.

* Its solution tinges the human skin of a purple colour.

An excess of a solution of POTASH poured in a solution of perchloride of gold produces at first no precipitate; after some time the liquor assumes a slightly greenish tinge, and a small black precipitate falls down[1].

* This effect, however, is solely owing to a small quantity of organic matter which the solution of potash contains. This insignificant black precipitate consists of metallic gold in an extreme state of division.

AMMONIA determines in solutions of perchloride of gold a yellow precipitate, * which is a compound of peroxyde of gold and of ammonia, (fulminating gold—aurate of ammonia).

A solution of CARBONATE OF POTASH produces no precipitate.

A solution of BICARBONATE OF POTASH produces no precipitate.

A solution of CARBONATE OF AMMONIA determines, in neutral solutions of perchloride of gold, a yellow precipitate similar to that produced by ammonia. Carbonic acid gas is disengaged.

A solution of PHOSPHATE OF SODA produces no precipitate.

A solution of OXALIC ACID produces a dark greenish-black colour, which is owing to the presence of metallic gold, and which requires a long time for precipitation. If the solution be heated, this effect is more promptly determined; and there is a visible disengagement of carbonic acid gas.

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[1] If the solution of gold be acid, it must be heated after the addition of potash or of ammonia, for these re-agents produce no precipitate in cold acid solutions of peroxyde of gold. If the solution contains ammoniacal salts, it must also be heated in order to obtain the precipitate.—ED.

A solution of FERROCYANURET OF POTASSIUM produces an emerald-green colour in solutions of perchloride of gold.

A solution of FERRICYANURET OF POTASSIUM produces no precipitate.

A solution of CYANURET OF MERCURY produces no precipitate.

A solution of SUBNITRATE OF MERCURY produces an immediate black precipitate.

A solution of PROTOSULPHATE OF IRON produces at first a blue colour in very dilute solutions of perchloride of gold; and afterwards a brown precipitate of metallic gold is formed. When the solution of perchloride of gold is not too dilute, an immediate brown precipitate of metallic gold is determined.

A solution of PROTOCHLORIDE OF TIN, to which enough muriatic acid has been added to render it clear, gives to an extremely dilute solution of perchloride of gold a purple colour; if the solution is more concentrated, this re-agent produces a deep purple precipitate (purple of cassius) insoluble in free muriatic acid.

A solution of IODIDE OF POTASSIUM produces a black colour in those of perchloride of gold, a yellowish-green precipitate of iodide of gold is deposited, and the liquid contains free iodine in solution.

* INFUSION OF GALLS produces in solutions of perchloride of gold a black precipitate of reduced gold, which, especially when heated, becomes brownish-yellow, and may be recognized as metallic gold.

HYDROSULPHURET OF AMMONIA gives in neutral solutions of perchloride of gold a dark precipitate of persulphuret of gold, completely soluble in an excess of re-agent[1].

Aqueous solution, or a current of SULPHURETTED HYDROGEN

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[1] The precipitate of persulphuret of gold produced by hydrosulphuret of ammonia is soluble, it is true, in an excess of this re-agent; but it must contain an excess of sulphur, otherwise it is not dissolved.—ED.

GAS, produces a black precipitate of persulphuret of gold in neutral and in acid solutions of perchloride of gold[1].

A bar of METALLIC ZINC plunged in solutions of gold precipitates the gold in the metallic state under the form of a voluminous brown coating.

The compounds of gold are decomposed by exposure to a red heat.

The neutral solution of gold reddens litmus paper.

Solutions of gold are easily detected by their behaviour towards solutions of PROTOSULPHATE OF IRON, of OXALIC ACID, and of PROTOCHLORIDE OF TIN.

There are some organic substances by which gold is reduced from the solution of perchloride of gold.

* There are, however, few organic substances which, like the INFUSION OF GALLS, can instantaneously operate this reduction. Most of them, in order to reduce the metal, must be heated for a long time with the solution of gold; and then there is generally only a small portion of the gold, which separates in the metallic form, with the characteristic yellow colour. But all organic substances, almost without exception, either volatile or not, provided there be a sufficient quantity present, completely reduce gold when, at the same time, a solution of potash is added. The addition of this alkali almost constantly determines an immediate deposition of gold under the form of a black precipitate; the black colour of which is so deep, that, judging by the colour, one could hardly conceive it to consist of the pure metal. This reduction occasionally requires a certain time for its production. There are only a few cases in which, though the alkali be added, it is necessary to heat the liquid in order to obtain the reduction of the gold; but the black precipitate is always more promptly determined with the help of heat.

* The formation of the precipitate which ammonia causes in solution of perchloride of gold is prevented by the presence

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[1] The persulphuret of gold thus produced is insoluble in simple acids, but soluble in aqua regia, and partly so in potash.—ED.

of some organic substances, for example, by a solution of gum arabic, and partly also by starch, but not by solution of either cane or grape sugar. If, however, the solution of the two latter substances remains for a long time in contact with the precipitate, the gold is partly reduced, especially with grape sugar.

* When, after having dissolved perchloride of gold in aqueous alcohol, the alcohol is driven off by the action of heat, the remaining aqueous solution gives an immediate yellow precipitate by pouring a solution of cyanide of mercury.

33. OXYDES OF TIN.

1°. PROTOXYDE OF TIN, SnO.

(Oxyde Stanneux.)

Pure protoxyde of tin is a powder, of a blackish-grey colour, which, when brought in contact with bodies in a state of ignition in the air, burns like tinder, and is thereby converted into deutoxyde of tin. Hydrate of protoxyde of tin is white, and more soluble in acids than protoxyde of tin is, after having been exposed to a red heat in close vessels.

* The salts of protoxyde of tin are colourless, and their solutions become easily oxydised when they are left exposed to the air. The protochloride of tin, which corresponds to the protoxyde, cannot be dissolved in water without being decomposed; a milky solution is thus produced, owing to the separation of an insoluble compound of protochloride and of protoxyde of tin.

* This solution likewise greedily absorbs the oxygen of the air, in consequence of which, when poured in certain metallic solutions, it has a strong deoxydising action, and reduces the metal[1].

* According to Regnault, protoxyde of tin, at a high temperature, decomposes water, with disengagement of hydrogen

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[1] For example, it reduces the persalts of iron to protosalts of iron, arsenic acid into arsenious acid, chromic acid into oxyde of chrome, &c., &c.—Ed.

gas, more easily than even metallic iron, and is thereby converted into deutoxyde of tin.

Solutions of protoxyde of tin in acids, and of protochloride of tin in water, when a sufficient quantity of muriatic acid has been added to render the solution clear, behave as follows towards re-agents:—

A solution of POTASH produces a white precipitate of hydrate of protoxyde of tin, soluble in an excess of alkali. After a time, but more rapidly by boiling, the solution undergoes a decomposition, in consequence of which metallic tin is precipitated in the form of a very voluminous black powder, and deutoxyde of tin combined with potash remains in solution.

AMMONIA determines in solution of protosalts of tin a white precipitate of hydrate of protoxyde of tin, insoluble in an excess of the re-agent.

A solution of CARBONATE OF POTASH produces a white precipitate of hydrate of protoxyde of tin, insoluble in an excess of the re-agent.

A solution of BICARBONATE OF POTASH, the same.

A solution of CARBONATE OF AMMONIA, the same.

A solution of PHOSPHATE OF SODA gives a white precipitate of phosphate of protoxyde of tin.

A solution of OXALIC ACID determines a white precipitate of oxalate of protoxyde of tin.

A solution of FERROCYANURET OF POTASSIUM produces a white gelatinous precipitate of ferrocyanuret of tin. * When this precipitate has a reddish tint, it is a proof that there was some copper in the solution.

A solution of FERRICYANURET OF POTASSIUM gives a white precipitate of ferricyanuret of tin, soluble in muriatic acid.

* INFUSION OF GALLS produces an abundant light yellowish precipitate in the milky solution of protochloride of tin, or in that to which only a little muriatic acid has been added.

HYDROSULPHURET OF AMMONIA produces in neutral solutions of protoxyde of tin a brown precipitate of protosulphuret of tin, soluble in a very large excess of the precipitant, especially when this re-agent is of recent preparation, and yellow from its containing an excess of sulphur. An excess of muriatic acid poured in this solution, produces a yellow precipitate of bisulphuret of tin mixed with sulphur.

An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, produces a dark brown precipitate of protosulphuret of tin, in neutral and in acid solutions of protosalts of tin[1].

A bar of METALLIC ZINC, plunged in solutions of protosalts of tin, precipitates tin in the metallic state, and in the form of whitish-grey spangles.

A solution of IODIDE OF POTASSIUM produces, in solutions of protosalts of tin, a white curdy precipitate, with a slight tinge of yellow, and which, after a certain time, when the liquor has been concentrated to a certain point, and * provided the quantity of iodide of potassium has been exactly proportioned to that of the protosalt of tin, partly becomes of a cinnabar red, and consists of proto-iodide of tin. By heating the whole, the proto-iodide of tin on cooling is deposited under the form of red needles. The precipitate is soluble in a great excess of iodide of potassium and in muriatic acid.

The behaviour of PERCHLORIDE OF GOLD towards protochloride of tin, and of other protosalts of tin, has been already noticed (page 170)[2].

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[1] The precipitate of protosulphuret of tin produced by sulphuretted hydrogen and hydrosulphuret of ammonia is soluble in potash and in alkaline sulphurets. A very large excess of hydrosulphuret of ammonia is required to dissolve it unless this re-agent contains an excess of sulphur, which may at once be done by adding a small quantity of sublimed sulphur well washed. Boiling nitric acid converts this protosulphuret into peroxyde of tin.—ED.

[2] An excess of perchloride of gold, from what has been said previously at page 170, produces in solutions of protoxyde and of protochloride of tin a purple precipitate (purple of cassius); but to obtain this effect, the liquor should contain some peroxyde of tin, wherefore a little *cold* nitric acid (the mixture must not be heated) should be added to peroxydise a portion of the protosalt of tin. An excess of a solution of protochloride of mercury (sublimate) produces in solutions of protochloride of tin a white precipitate of subchloride of mercury (calomel), because the protochloride of tin takes up half the chlorine of the protochloride of mercury; the result being, therefore, that the protochloride of tin becomes a perchloride of tin, whilst the protochloride of mercury (sublimate) becomes a subchloride of mercury (calomel).—ED.

The protosalts of tin are decomposed by exposure to a red heat in contact with the air.

Their solutions redden litmus paper.

The protosalts of tin, which are insoluble in water, are nearly all soluble in muriatic acid, at least provided they have not been previously ignited. The presence of protoxyde of tin is detected in these solutions by pouring in them a solution of sulphuretted hydrogen, or a solution of gold.

Before the BLOW-PIPE, protosalts of tin, mixed with soda, yield metallic tin, when heated upon charcoal in the interior flame. The globule of reduced tin may be recognized, because it may be flattened under the hammer, and because when mixed with a green bead of microcosmic salt, holding protoxyde of copper in solution, the bead becomes opaque, or of a reddish-brown colour in the exterior flame, which phenomenon is due to the reduction of the protoxyde into suboxyde of copper.

Solutions of protosalts of tin are very easily recognized by their behaviour towards solution of gold (page 170).

The presence of non-volatile ORGANIC SUBSTANCES may sometimes hinder the precipitation of protoxyde of tin by alkalies.

2°. SESQUIOXYDE OF TIN, Sn_2O_3.

(Oxyde Sustanneux.)

* THE sesquioxyde of tin obtained by decomposing hydrate of peroxyde of iron by means of a solution of protochloride of tin, is white, but ordinarily it has a yellowish colour, which is imparted to it by a certain quantity of peroxyde of iron, which remains mixed with it: it has a very mucilaginous consistency, and on that account it is difficult to collect it on a filter. In the anhydrous state it forms a powder of a greyish-brown colour. Heated in contact with the air, it is converted into peroxyde of tin. Whilst still moist, it is soluble in ammonia: in this it differs from protoxyde of tin, which is insoluble in that re-agent; it is difficultly soluble in dilute muriatic acid, but more easily so in the concentrated acid. The solution, like that of protoxyde of tin, gives a precipitate of purple of

cassius, when a solution of perchloride of gold is poured into it. This character distinguishes it from peroxyde of tin, which is not precipitated by perchloride of gold.

3°. PEROXYDE OF TIN, SnO_2.

[DEUTOXYDE OF TIN.]

(*Oxyde Stannique.*)

PURE peroxyde of tin is white or yellowish after ignition. The native peroxyde is generally of a darker hue, owing to some foreign substances with which it is accidentally mixed. After ignition, it becomes altogether insoluble in acids, and must be fused with an excess of carbonate of potash, or of soda, in order to become again soluble in those re-agents. In the pure state, it is infusible, except by a very violent heat, but it easily fuses into an enamel when heated with basic substances. The hydrated peroxyde of tin, which has been obtained by treating tin by nitric acid, is white and insoluble, even with the help of heat, in almost all acids, particularly sulphuric and nitric acids. * It is likewise perfectly insoluble in somewhat concentrated muriatic acid, even at a boiling heat. When, however, after treatment with this acid, it is left standing, the oxyde is deposited, and by decanting the supernatant acid, the peroxyde which has remained undissolved, and had combined with the acid without being able to dissolve in an excess thereof, is totally soluble in pure water. If such a solution be boiled, the peroxyde of tin is separated, and after cooling it is no longer soluble in the liquor[1].

* The aqueous solution of this hydrated perchloride of tin, the solution of the volatile perchloride of tin (Libavius' fuming liquor), and even the solutions in acids of the peroxyde of tin which has been precipitated by ammonia from an aqueous solution of perchloride of tin, differ from each other in their deportment towards re-agents. The latter solution behaves towards re-agents like an aqueous solution of perchloride of tin. The

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[1] It is believed that these peculiarities are referrible to changes in the state of hydration.—ED.

hydrate of peroxyde of tin, which has been precipitated by ammonia from an aqueous solution of perchloride of tin, and which has been dried (an operation during which heat should be eschewed), differs already by its exterior characters from the peroxyde of tin prepared with nitric acid. It consists of translucid fragments, with a vitreous fracture, whilst the latter is pulverulent. After ignition the two oxydes behave exactly in the same manner. Both are then entirely insoluble in acids.

* Solution of perchloride of tin is not decomposed by a prolonged ebullition. Even though a considerable quantity of nitric acid be added, and the whole boiled for a long time, no insoluble peroxyde of tin is precipitated, but when the solution of perchloride of tin, mixed with nitric acid, has been brought by boiling to a rather high degree of concentration, then an abundant disengagement of nitrous vapours takes place, and an insoluble precipitate of peroxyde of tin is formed.

A solution of POTASH produces in solution of perchloride of tin a bulky white precipitate of hydrated peroxyde of tin, soluble with extreme facility in a slight excess of the re-agent, and the solution does not become turbid even after a long time.

* The hydrate of peroxyde of tin produced by the oxydising agency of nitric acid, dissolves partly only in an excess of potash; the solution, after a long space of time, spontaneously deposits a great quantity, but not the whole, of the peroxyde of tin which it contained, so that it yet retains a great deal of it. A solution of potash, poured in an aqueous solution of hydrated perchloride of tin, produces a white precipitate sparingly soluble in an excess of the re-agent, even if it be boiled with it.

AMMONIA determines in solutions of perchloride of tin a bulky white precipitate of hydrate of peroxyde soluble in a great excess of the re-agent. * Yet the solution always remains slightly turbid; in course of time it becomes clear; but it afterwards deposits an abundant and bulky precipitate. The precipitate, which ammonia thus determines, is easily dissolved by all acids, even by nitric acid. The peroxyde of tin, produced by the oxydising agency of nitric acid, is not soluble in ammonia: the aqueous solution of the hydrated chloride formed by this peroxyde, in which ammonia is poured, gives a white precipitate very slightly soluble in an excess of the re-agent.

A solution of CARBONATE OF POTASH determines in solution of perchloride of tin a white precipitate of hydrate of peroxyde, accompanied by a disengagement of carbonic acid gas, and which precipitate is completely soluble in an excess of the re-agent; yet, after a time, a white precipitate is again deposited in this last solution, from which the peroxyde of tin is thus ultimately separated *in toto*.

* The peroxyde produced by nitric acid does not dissolve in a solution of carbonate of potash.

* A solution of carbonate of potash poured in the aqueous solution of the hydrated perchloride of that oxyde produces a white bulky precipitate insoluble in an excess of the re-agent.

A solution of BICARBONATE OF POTASH produces in solutions of perchloride and of peroxyde of tin a white precipitate of hydrate of peroxyde of tin, which is insoluble in an excess of the re-agent; the formation of this precipitate is accompanied by a disengagement of carbonic acid gas.

A solution of CARBONATE OF AMMONIA behaves in the same manner.

A solution of PHOSPHATE OF SODA produces a white precipitate of phosphate of tin.

A solution of OXALIC ACID produces no precipitate in neutral solutions of perchloride and of peroxyde of tin.

A solution of FERROCYANURET OF POTASSIUM produces no immediate precipitate in these solutions, but after a time a white turbidness appears, and by long standing the whole liquor congeals into a thick, stiff, yellowish jelly which is insoluble in muriatic acid. A solution of ferrocyanuret of potassium requires a much longer time to produce the jelly in solutions of persalts of tin when they are dilute.

A solution of FERRICYANURET OF POTASSIUM produces no precipitate in solutions of persalts of tin.

* INFUSION OF GALLS produces no immediate precipitate in

neutral solutions of perchloride and of peroxyde of tin, but in course of time the mixture congeals into a jelly, especially with the solutions of perchloride.

HYDROSULPHURET OF AMMONIA produces in neutral solutions of perchloride and of peroxyde of tin, a yellow precipitate of bisulphuret of tin. This precipitate is completely soluble in an excess of the re-agent.

* This precipitate is soluble also in ammonia, in solution of pure potash, and of carbonate of potash; in solutions of pure potash and of carbonate of potash peroxyde of tin is deposited[1].

An aqueous solution or a current of SULPHURETTED HYDROGEN GAS does not produce immediately any precipitate in neutral or in dilute acid solutions of peroxyde of tin. After a time, however, a yellow precipitate of bisulphate of tin is produced, which augments by long standing. This yellow precipitate is more rapidly formed when solution of peroxyde of tin is boiled in conjunction with aqueous solution of sulphuretted hydrogen[2].

* The colour of this precipitate bears some analogy with that produced by sulphuretted hydrogen in solutions of arsenious acid, and, like the arsenical sulphuret, it is soluble in solutions of potash and of ammonia. But it differs from the precipitate of sulphuret of arsenic because it is not completely volatilisable by heat, and because when kept red hot in contact with the air, for a sufficient length of time, it becomes converted into peroxyde of tin.

A bar of METALLIC ZINC plunged in solutions of perchloride or of peroxyde of tin produces, under disengagement of hydrogen gas, a white gelatinous precipitate, which is peroxyde of tin[3].

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[1] Acids reprecipitate the yellow bisulphuret from these solutions in an unaltered condition.—ED.

[2] The bisulphuret thus formed is soluble in potash and in the alkaline sulphurets, and also in concentrated muriatic acid. According to Dr. Fresenius, it is soluble also, but with difficulty, in pure ammonia and in carbonate of ammonia. Nitric acid converts it into insoluble peroxyde of tin. Boiled with oxyde of copper, sulphuret of copper is produced, and peroxyde of tin remains dissolved in the solution of potash.—ED.

[3] If the solution contains no free nitric acid, metallic tin in the shape of scales of a grey colour or of a spongy mass is deposited.—ED.

A solution of IODIDE OF POTASSIUM produces no precipitate in these solutions.

A solution of PERCHLORIDE OF GOLD produces no precipitate.

The persalts of tin are decomposed when heated to redness.

Their solutions redden litmus paper.

The compounds of peroxyde of tin, which are insoluble in water, can ordinarily be dissolved in muriatic acid, provided they have not been ignited. The presence of peroxyde of tin in these acid solutions is principally detected by the yellow precipitate which sulphuretted hydrogen determines therein, and which is soluble in hydrosulphuret of ammonia. When the compound of peroxyde of tin has been ignited, and thereby rendered insoluble in muriatic acid, it is to be fused in a platinum crucible with double or treble its weight of dry carbonate of potash or of soda, and the fused mass is to be dissolved in dilute muriatic acid; peroxyde of tin may now be recognised in this solution by means of the re-agents mentioned above. It will be immediately perceived that this method is applicable only when the peroxyde of tin is combined with an acid, which cannot be precipitated by sulphuretted hydrogen. The blow-pipe is, however, a more easy process to detect the presence of peroxyde of tin in these insoluble compounds.

Before the BLOW-PIPE the persalts, like the protosalts of tin, are reduced into metallic tin.

Solutions of persalts of tin are easily recognised by their behaviour towards sulphuretted hydrogen and hydrosulphuret of ammonia. But compounds of persalts of tin are best distinguished from arsenites and arseniates by means of the blow-pipe.

The presence of non-volatile ORGANIC SUBSTANCES may sometimes hinder the precipitation of peroxyde of tin by alkalies.

34. OXYDE OF ANTIMONY, Sb_2O_3.

[SESQUIOXYDE OF ANTIMONY.]

(*Oxyde Antimonique.*)

PURE oxyde of antimony is white—exposed to a gentle red heat it fuses into a yellow mass, which, on cooling, has a white and crystalline appearance. Heated in close vessels it may be completely sublimed, and it is condensed into shining needles. Heated in contact with the air, it emits a white smoke, and is partly converted into antimonious acid. Heated in conjunction with charcoal it is easily reduced into metallic antimony. When heated with sulphuret of antimony it easily combines with it and produces a red glass. It is insoluble in nitric acid, *but not altogether so, for the acid liquor which has been left for a long time in contact with it always contains a small quantity of it. Muriatic acid dissolves it, but the solution becomes milky by adding water; a bulky combination, which is a basic chloride that is a compound of oxyde and of chloride of antimony, is then separated, and in course of time it reaches the bottom of the vessel[1]. If enough muriatic acid be added to the milky liquor to render it clear, nitric acid does not precipitate it.

* When nitric acid is added to a solution of antimony, which has been rendered milky by the addition of water, it becomes limpid; yet, after long standing, the mixture becomes somewhat turbid.

A solution of protochloride of antimony, which has been rendered clear by addition of a sufficient quantity of muriatic acid, behaves towards re-agents as follows:—

A solution of POTASH produces a voluminous precipitate of oxyde of antimony, † completely soluble in a large excess of the re-agent.

* If potash be not added in sufficient quantity to dissolve the bulky precipitate, and if the whole be left for a long time, the precipitate is deposited at the bottom of the vessel, its bulk

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[1] An acid chloride will remain in solution.—ED.

diminishes, and crystalline grains, which are a combination of oxyde of antimony and potash, are deposited on the sides of the vessel. The liquor after having been separated from the precipitate by filtering, retains still much oxyde of antimony; but the smaller the excess of potash employed, the less also is the quantity of oxyde of antimony retained in solution.

AMMONIA forms, in solutions of oxyde of antimony, an abundant and bulky precipitate, which after some time settles at the bottom of the vessel.

* This precipitate is not soluble in an excess of the re-agent, for the liquid which is filtered therefrom contains no trace of oxyde of antimony.

A solution of CARBONATE OF POTASH throws down a bulky precipitate which, after a time, settles at the bottom.

† * An excess of the re-agent redissolves a small portion of oxyde of antimony.

† A solution of BICARBONATE OF POTASH behaves in the same manner.

* A solution of CARBONATE OF SODA acts in the same manner, only by standing; oxyde of antimony separates still more completely from the liquor, so that after filtering it contains none.

A solution of CARBONATE OF AMMONIA behaves in the same manner.

* A solution of PHOSPHATE OF SODA produces in solutions of oxyde of antimony an abundant bulky precipitate, which does not settle even after a long time. The filtered liquid contains still a large quantity of oxyde of antimony in solution.

A solution of OXALIC ACID produces an abundant and bulky white precipitate, which in time settles at the bottom of the vessel.

* After a long time, the oxyde of antimony is so completely precipitated by oxalic acid, that no trace of it can be found in the filtered liquid. When too much oxalic acid is added, the precipitate does not immediately appear, but only after a certain time. In either case the oxyde of antimony is separated from the liquor.

A solution of FERROCYANURET OF POTASSIUM produces a white precipitate insoluble in muriatic acid, and which consequently is not occasioned by the water of the re-agent.

A solution of FERRICYANURET OF POTASSIUM does not determine any precipitate; should a slight turbidness be produced, it is dissipated by a small quantity of muriatic acid, and this turbidness is probably occasioned only by the water of the re-agent.

* INFUSION OF GALLS produces a white or slightly yellowish precipitate.

HYDROSULPHURET OF AMMONIA produces a red[1] precipitate of sulphuret of antimony, completely soluble in an excess of the re-agent.

* The application of heat promotes this redissolution, which is more easily effected also when the hydrosulphuret of ammonia is yellow, and has been prepared for some length of time, or when some finely levigated sulphur has been added to it. If the solution of oxyde of antimony contains other metallic oxydes, such as, for example, oxydes of iron, of lead, of copper, &c., they are of course precipitated, and separated as black insoluble sulphurets, whilst the sulphuret of antimony dissolves in the excess of the re-agent.

An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, causes a red[2] precipitate of sulphuret of antimony in acid, and in neutral solutions of sesquisalts of antimony. If the solution of antimony is neutral and diluted, the effect of sulphuretted hydrogen at first is to impart to it a red colour without producing any precipitate; but by adding muriatic acid, or merely heating the liquor, a precipitate immediately appears[3].

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[1] The precipitated sulphuret of antimony is orange-red.—ED.

[2] Orange-red.—ED.

[3] The protosulphuret of antimony thus precipitated is readily soluble in potash, and consequently sulphuretted hydrogen cannot form a precipitate in alkaline solutions; or, at any rate, the whole of the antimony cannot be thus precipitated. Protosulphuret of antimony is also soluble in the alkaline sulphurets and in concentrated boiling muriatic acid, with evolution of sulphuretted hydrogen gas. If oxyde of copper be put in the solution of sulphuret of antimony in potash, and the whole boiled together, the result will be a precipitate of sulphuret of copper, and oxyde of antimony will remain dissolved in the potash.—ED.

A bar of METALLIC ZINC, plunged in solution of antimony, precipitates antimony in the metallic state, under the form of a black powder[1].

The sesquisalts of antimony cannot be calcined in contact with the air, without being volatilised or decomposed.

Their solutions are always acid, and redden litmus paper.

Almost all the combinations of sesquioxyde of antimony, which are insoluble in water, are soluble in muriatic acid. Sulphuretted hydrogen is the best re-agent for detecting the presence of oxyde of antimony in such a solution; and the acid with which the oxyde was combined may be discovered in the liquid filtered from the sulphuret of antimony produced. If the insoluble combination consisted of oxyde of antimony and of a base, that base is also contained in this filtered liquid in the state of a chloride.

Before the BLOW-PIPE, the salts of antimony being mixed with soda are reduced in the interior flame into metallic antimony, which after fusion continues for a long time to emit thick white fumes, and when these white fumes cease, the metallic bead becomes covered with a network of crystals, which consist of oxyde of antimony; * the charcoal is covered with a white fur.

The behaviour of oxyde of antimony towards the solution of sulphuretted hydrogen, and hydrosulphuret of ammonia, is its most distinctive character.

* The presence of organic substances may modify the deportment of re-agents towards solutions of oxyde of antimony, in various ways. Several of these substances hinder the precipitation of the oxyde by water. This is always the case when non-volatile organic acids are added to the solutions. Volatile organic substances, such as alcohol, either pure or containing ether, do not prevent the solution of oxyde of antimony from turning milky.

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[1] If the solution contains free muriatic or sulphuric acid in sufficient quantity to produce a rapid evolution of hydrogen gas, the gas in the nascent state combines with a portion of the reduced antimony, and forms antimoniated hydrogen; about which more will be said when we come to the detection of arsenic. If the solution contains free nitric acid, the reduced antimony is mixed with oxyde of antimony.—ED.

* Tartaric acid is the organic substance which, even in small quantity, more particularly prevents a solution of antimony from being decomposed by water. But its influence does not stop there; it also changes the mode of action of almost all the other re-agents. As it frequently happens, in analytical researches, that oxyde of antimony is met with dissolved in the state of tartrate of antimony and potash (tartar emetic), it is important to know the behaviour of this salt towards re-agents.

* The aqueous solution of tartar emetic is perfectly limpid, and not milky, owing to the presence of tartaric acid.

* A small quantity of solution of POTASH, poured in a solution of tartar emetic, produces an immediate white precipitate of oxyde of antimony, completely and easily soluble in an excess of the re-agent.

* AMMONIA, even in large quantity, does not at once determine any turbidness; but after a time a white precipitate is produced, which is insoluble in an excess of the re-agent. When the whole has been left at rest for a very long time, the liquid which is separated from the precipitate by filtering contains some oxyde of antimony, though not much.

* A solution of CARBONATE OF POTASH produces, not at once, but only after a time, a white precipitate of oxyde of antimony insoluble in an excess of the re-agent. The liquid which is filtered from this precipitate still retains much oxyde of antimony.

* A solution of BICARBONATE OF POTASH behaves almost in the same manner.

* A solution of CARBONATE OF SODA, ditto.

* A solution of CARBONATE OF AMMONIA, ditto.

* A solution of PHOSPHATE OF SODA produces no precipitate in that of tartar emetic, even after a long time.

* A solution of OXALIC ACID produces a precipitate only after a long time; this precipitate is inconsiderable and insoluble in an excess of the re-agent; the liquid filtered therefrom retains still much oxyde of antimony.

* A solution of MURIATIC ACID poured in small quantity in

one of tartar emetic, at once produces an abundant precipitate, most easily soluble in an excess of the re-agent.

* Nitric acid, likewise, determines a precipitate, but which is insoluble in an excess of the acid. The liquid filtered therefrom retains still some oxyde of antimony.

* Sulphuric acid (diluted) produces a precipitate which is insoluble in an excess of acid. The liquid filtered from the precipitate contains much oxyde of antimony.

* Acetic acid does not trouble the solution of tartar emetic;

* Tartaric acid, the same.

* A solution of ferrocyanuret of potassium produces no precipitate.

* A solution of ferricyanuret of potassium produces no precipitate.

* Infusion of galls at once produces an abundant, bulky, whitish-yellow precipitate.

* Hydrosulphuret of ammonia determines a red precipitate of sulphuret of antimony, which an excess of the re-agent redissolves under the same conditions as that which it produces in other solutions of oxyde of antimony, (page 183).

* Aqueous solution, or a current of sulphuretted hydrogen gas, produces no precipitate in dilute solutions of tartar emetic. In such cases the solution only assumes a deep-red colour, and the red precipitate of sulphuret of antimony appears only when a small quantity of some acid is added, or when the liquid is heated, or else when it is left for a long time at rest.

* The precipitate of sulphuret of antimony, which sulphuretted hydrogen determines in solutions of oxyde of antimony, may acquire another colour from the presence of several organic substances. † For example, when albuminous liquids have been added to a solution of tartar emetic, the solution of sulphuretted hydrogen gives a yellow colour; and if any portion, however small, of an acid be added, a voluminous yellow precipitate is produced, which remains suspended for a long time.

* We shall treat of antimonious and antimonic acids, which are two higher degrees of oxydation of antimony, in the section on acids.

35. OXYDES OF MOLYBDENUM.

1°. PROTOXYDE OF MOLYBDENUM, MoO.

(Oxyde Molybdeux.)

* The hydrate of protoxyde of molybdenum is black when it has been obtained by precipitating it by means of an excess of ammonia, the solution of an alkaline molybdate first rendered acid by the addition of muriatic acid, and then treated by zinc, [according to the method indicated by Berzelius]. Heated in contact with the air, it is converted into molybdic[1] acid. It is very soluble in muriatic acid; the solution is of a very deep black colour; diluted with much water, it is brown. This solution behaves towards re-agents in the following manner:—

* A solution of POTASH produces a brownish-black precipitate of hydrate of protoxyde of molybdenum, insoluble in an excess of the re-agent.

* AMMONIA, the same.

* A solution of CARBONATE OF POTASH gives a blackish-brown precipitate of hydrated protoxyde of molybdenum, slightly soluble in an excess of the re-agent.

* A solution of BICARBONATE OF POTASH behaves in the same manner.

* A solution of CARBONATE OF AMMONIA also determines a blackish-brown precipitate of hydrate of protoxyde of molybdenum, completely soluble in an excess of the re-agent.

* A solution of PHOSPHATE OF SODA produces a blackish-brown precipitate of phosphate of protoxyde of molybdenum.

* A solution of OXALIC ACID gives no precipitate.

* A solution of FERROCYANURET OF POTASSIUM, and

A solution of FERRICYANURET OF POTASSIUM, both determine a precipitate of a reddish-brown colour.

* HYDROSULPHURET OF AMMONIA produces, in solutions of

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[1] The hydrate of protoxyde of molybdenum thus recently precipitated is black, but whilst being washed on the filter its colour becomes lighter and brownish, which is due to an incipient degree of higher oxydisation.—ED.

protosalts of molybdenum, previously saturated with ammonia, a brownish-yellow precipitate of sulphuret of molybdenum, which, if the solution of protosalt of molybdenum contains no oxyde of zinc, is completely soluble in an excess of the re-agent[1].

* An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, does not at first produce any precipitate in solutions of protosalts of molybdenum; but after a time a blackish-brown precipitate appears, which is sulphuret of molybdenum.

* The combinations of protoxyde of molybdenum with the acids, which in a free state are very volatile, are decomposed by exposure to a red heat in contact with the air, and the protoxyde of molybdenum becomes then converted into molybdic acid.

* Before the BLOW-PIPE, protoxyde of molybdenum is recognised, because it communicates to microcosmic salt, when fused upon a wire of platinum in the interior flame, a fine green colour, which is more distinct after cooling. In the exterior flame the colouring is more feeble, and cannot be preserved so well after cooling. Protoxyde of molybdenum, treated with borax in the interior flame of the blow-pipe, dissolves therein, and communicates to the fused bead, not a green, but a reddish-brown colour. Treated with soda upon charcoal it is reduced into metallic molybdenum, which may be obtained, under the form of a metallic grey powder, by washing off the charcoal.

* The compounds of protoxyde of molybdenum are more principally distinguished from other substances by their behaviour before the blow-pipe. Thus treated they differ from the compounds of copper, because, after addition of tin, they do not communicate a brown colour to microcosmic salt; from the compounds of iron, because, in the exterior flame, they do not give a reddish-brown colour to microcosmic salt; from the oxydes of uranium, because these, when heated with borax

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[1] Oxyde of zinc not being soluble in any excess of hydrosulphuret of ammonia. —ED.

in the exterior flame, give it a colour which is sensibly yellow. But besides this, in analysis in the humid way, the protosalts of molybdenum may be very well distinguished by the dark colour of their solution, which character has some analogy with those of sesquioxyde of manganese; but they are more especially recognised by the precipitate produced by hydrosulphuret of ammonia, which precipitate is easily soluble in an excess of the re-agent, a character which perfectly identifies the molybdous combinations from the other compounds which it may resemble.

2°. DEUTOXYDE OF MOLYBDENUM, MoO_2.

(*Oxyde Molybdique.*)

* Deutoxyde of molybdenum is obtained in the dry way by heating to redness an alkaline molybdate with muriate of ammonia, and treating the mass by water. Deutoxyde of molybdenum is blackish-brown, and insoluble in acids. It is, however, possible that it may contain a certain quantity of molybdenum. The hydrate of deutoxyde of molybdenum is brown and bulky, soluble in acids, to which it imparts a brownish colour; it is also slightly soluble in pure water[1]; this solution has a brownish colour, and feebly reddens litmus paper, yet, in order to precipitate the hydrate from such a solution, it suffices to dissolve a salt, for example sal ammoniac, therein. When moist hydrate of deutoxyde of molybdenum is left exposed to the air for a long time, it absorbs oxygen, and its surface becomes green or blue, whilst the water which is poured upon it assumes a green colour. The corresponding deutochloride of molybdenum is obtained by heating metallic molybdenum in an atmosphere of chlorine gas. In the dry state it has a metallic lustre, and a black colour; it fuses at a gentle heat, and is volatilised under the form of a deep red gas. This chloride is

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[1] But it is insoluble in saline solutions. It should therefore be washed with a solution of sal ammoniac, which salt may afterwards be removed by alcohol. Yet hydrate of deutoxyde of molybdenum is slightly soluble in solution of sal ammoniac, but much less so than in pure water.—Ed.

soluble in water[1]. The concentrated aqueous solution has a black colour, which becomes brown, and lastly, yellow, by addition of water. If, however, the deutochloride of molybdenum contains any trichloride, which is the case when the metallic molybdenum which has been treated by gaseous chlorine contained a little deutoxyde of molybdenum, it dissolves in water, to which it communicates a fine blue colour.

* Solution of deutoxyde of molybdenum in acids behaves in the following manner towards re-agents:—

* A solution of POTASH produces a voluminous brownish-black precipitate of hydrate of deutoxyde of molybdenum, insoluble in an excess of the re-agent[2].

* AMMONIA behaves in the same manner.

* A solution of CARBONATE OF POTASH produces a light-brown precipitate of hydrate of deutoxyde of molybdenum, soluble in an excess of the re-agent[3].

* A solution of BICARBONATE OF POTASH produces a light-brown precipitate, soluble in an excess of the re-agent.

* A solution of CARBONATE OF AMMONIA, the same[4].

* A solution of PHOSPHATE OF SODA gives a brownish-white precipitate of phosphate of deutoxyde of molybdenum.

* A solution of OXALIC ACID produces no precipitate.

* A solution of FERROCYANURET OF POTASSIUM gives a brown precipitate.

* A solution of FERRICYANURET OF POTASSIUM gives a brown precipitate.

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[1] Deutochloride of molybdenum dissolves in water with so much violence that the liquid appears as if it were boiling, and effervesces as if a gas were disengaged, which however is not the case.—ED.

[2] When alkalies are added to a neutral solution of deutoxyde of molybdenum in acids, it generally occurs that the immediate precipitate which is then formed is redissolved. This is owing to hydrate of deutoxyde of molybdenum being soluble in water, from which it is precipitated only when the liquid is mixed with a sufficient quantity of the salt by which it is displaced.—ED.

[3] Berzelius says, when a solution of deutoxyde of molybdenum in carbonate of potash contained in an open vessel is thus left to itself, it gradually assumes another colour and becomes transformed into a molybdate.—ED.

[4] According to Berzelius, the solution of hydrate of deutoxyde of molybdenum in carbonate of ammonia is entirely precipitated by ebullition.

* HYDROSULPHURET OF AMMONIA produces, in solution of deutoxyde of molybdenum saturated with ammonia, a brownish-yellow precipitate of sulphuret of molybdenum, soluble in an excess of the re-agent, and which is precipitated from such a solution by muriatic acid.

* An aqueous solution, or a current of SULPHURETTED HYDROGEN GAS, at first yields no precipitate; but after some time a brown precipitate of sulphuret of molybdenum is formed.

* Before the BLOW-PIPE, deutoxyde of molybdenum behaves like the protoxyde.

* The combinations of deutoxyde of molybdenum are distinguished from other combinations which they may resemble, by the same characters which have been mentioned in reference to the protoxyde of molybdenum; but the combinations of proto and of deutoxyde of molybdenum are with difficulty distinguished from each other, because both behave nearly in the same manner with most re-agents. The best method of establishing a distinction between them consists in taking into consideration the solubility of protoxyde of molybdenum in carbonate of potash, which is greater than that of the deutoxyde in this re-agent[1].

* When we come to treat of acids, we shall have occasion to speak of the highest degree of oxydisation of molybdenum, namely, molybdic acid, and of its blue combinations with deutoxyde of molybdenum.

36. OXYDE OF TUNGSTEN, WO_2.[2]

[DEUTOXYDE OF TUNGSTEN.]

(*Oxyde Tungstique.*)

* OXYDE of tungsten is obtained in the dry way, by treating alkaline tungstates with muriate of ammonia, and treating the

mass by water after it has been exposed to a red heat. It has a black colour: sometimes, however, it is yellowish; but in such a case it is ordinarily combined with some alkali. When strongly heated in contact with the air, it absorbs oxygen, and is converted into tungstic acid. It does not dissolve in acids, and in general it appears not to have the power to combine with them.

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[1] According to Berzelius, the salts of deutoxyde of molybdenum, which are insoluble in water, dissolve by degrees in an alkaline solution, as the oxyde becomes gradually converted into an acid, a phenomenon which does not take place if the liquid contains no alkali.—ED.

[2] The atomic symbol W for Tungsten, is taken from the name Wolfram, from the German appellation of the mineral in which it was found.—ED.

* Before the BLOW-PIPE, oxyde of tungsten may be recognised by the fine blue colour which it communicates to microcosmic salt in the interior flame; this colour generally disappears in the exterior flame, especially by fusing the bead upon a wire of platinum. When oxyde of tungsten contains iron, the bead acquires a blood-red colour in the interior flame. Borax is not coloured blue by oxyde of tungsten in the interior flame; it only becomes yellow or red. When oxyde of tungsten is treated with a little soda upon charcoal in the interior flame of the blow-pipe, a grey powder is obtained, which is metallic tungsten. After removing the charcoal by levigation, if more soda be added, a combination of oxyde of tungsten with soda is often obtained, which has a yellow colour, and a metallic lustre.

* The higher degree of oxydisation of tungsten will be spoken of when we come to acids.

37. OXYDES OF VANADIUM.

* THE reactions indicated in this article are extracted from the Memoir of Berzelius upon Vanadium.

1°. PROTOXYDE OF VANADIUM, VO.

(Sousoxyde de Vanadium.)

WHEN protoxyde of vanadium has been obtained by the reduction of vanadic acid by means of hydrogen gas, with the help of a red heat, it is black, and has a semi-metallic lustre. It is infusible; heated in the air it ignites, burns like tinder, and is converted into black oxyde. Exposed to the air it begins after a short time to oxydise, and if it then be thrown into water, the liquid turns green, a phenomenon which takes place so much the more rapidly, as the temperature at which the reduction of the oxyde has been effected was less elevated. Acids and alkalies do not dissolve protoxyde of vanadium; yet when it is left for a long time in contact with these re-agents it produces compounds of deutoxyde of vanadium with the acid or the alkali which has been employed, and thereby the water becomes, of course, coloured. Acids do not dissolve protoxyde of vanadium, even at a boiling heat. We must, however, except nitric acid, which dissolves it, assuming at the same time a blue colour, and disengaging nitric oxyde gas.

2°. DEUTOXYDE OF VANADIUM, VO_2.

(Oxyde Vanadique—Acide Vanadeux.)

* **Obtained** in the dry way, deutoxyde of vanadium is black, of an earthy appearance, and is infusible at the temperature at which glass softens. Hydrate of deutoxyde of vanadium is a whitish-grey light mass which settles with difficulty in water. When the contact of the air has been avoided whilst drying it, it retains its grey colour after exsiccation; but if this precaution has not been taken it has a slightly bluish tinge. This effect is likewise produced when the dry oxyde is kept in vessels containing atmospheric air. The hydrate obtained by the precipitation of the solution of its salts by means of solution of carbonate of soda always contains a little carbonic acid; this carbonic acid is only in very minute quantity, and does not appear to be an essential constituent.

* Deutoxyde of vanadium combines both with acids and with bases. With acids it forms salts of deutoxyde of vanadium. The hydrate of deutoxyde of vanadium is more easily dissolved by acids than the ignited oxyde; in the latter case, the solution is slowly though completely effected. When ignited, deutoxyde of vanadium contains a little vanadiate of deutoxyde of vanadium; muriatic acid dissolves it with disengagement of chlorine.

* Solution of salts of vanadium in water has a fine blue colour, though not very deep. That of bichloride of vanadium is blue, but sometimes it is brown. The solutions of several

salts of deutoxyde of vanadium become green when left exposed to the air. They have a sweetish astringent taste, precisely like that of solutions of protosalts of iron.

* The solutions of the pure FIXED ALKALIES and of the pure FIXED ALKALINE CARBONATES produce in solution of deutosalts of vanadium a whitish-grey precipitate of hydrate of deutoxyde of vanadium, soluble in an excess of alkali. The solution has a brown colour. A larger excess of alkali produces a brown precipitate of an alkaline vanadite, soluble in pure water, to which it communicates a brown colour, but is only slightly soluble in an alkaline water.

* Solutions of ALKALINE BICARBONATES produce also in those of deutosalts of vanadium a grey precipitate of hydrate of deutoxyde of vanadium, soluble in an excess of the re-agent; the solution has a pale blue colour.

* AMMONIA in excess produces also a brown precipitate, which forms, it is true, a brown solution with pure water, but which is completely insoluble when the water contains ammonia, owing to which the supernatant liquor of the precipitate is colourless.

* A solution of FERROCYANURET OF POTASSIUM determines also a yellow precipitate in solutions of deutosalts of vanadium; this precipitate is a ferrocyanuret of vanadium, insoluble in acids, and which turns green by contact with the air.

* A solution of FERRICYANURET OF POTASSIUM determines the formation of a green gelatinous mass, which is ferricyanuret of vanadium.

* HYDROSULPHURET OF AMMONIA determines in solutions of deutoxyde of vanadium a blackish-brown precipitate of sulphuret of vanadium, soluble in an excess of the re-agent: the solution has a dark purple colour.

* SULPHURETTED HYDROGEN GAS does not create any precipitate in either neutral or acid solutions of deutoxyde of vanadium.

* INFUSION OF GALLS communicates to solutions of deutoxyde of vanadium a blue colour so intense that they appear like

ink. If the liquid be left at rest, a voluminous black precipitate of tannate of vanadium is formed, and the liquid is translucid, and slightly bluish.

The salts of deutoxyde of vanadium, in the solid form, are dark blue; some of them, however, are of a light-blue colour. Most of them are soluble in water. The subsalts and the anhydrous salts are brown, but give a blue colour to the water in which they are dissolving.

The behaviour of deutoxyde of vanadium before the blow-pipe is the same as that of vanadic acid, and will be treated of under this head, as also the means by which the combination of this oxyde can be distinguished from other substances.

38. OXYDE OF CHROMIUM, Cr_2O_3.

[SESQUIOXYDE OF CHROMIUM.]

(*Oxyde Chromique.*)

Hydrate of oxyde of chromium is greenish-grey. It is easily soluble in acids, and the solution, even dilute, has a deep emerald green colour; when, however, it is seen through transmitted artificial light, it appears of a violet colour. Hydrate of oxyde of chromium loses its water when submitted to heat. When it begins to attain a red heat, it suddenly becomes ignited with a vivid light[1]. The colour of the oxyde is dark green. After ignition, it is insoluble in acids except [concentrated] sulphuric acid, which dissolves it with the help of heat[2].

* Salts of oxyde of chromium are green, or of a deep purple colour, such as for example, that of chrome alum, which is a double salt, produced by the combination of sulphate of potash

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[1] This phenomenon takes place in closed as well as in open vessels, and is not attended with either gain or loss of weight. After cooling it is of a grass-green colour, and insoluble in the acids, except concentrated sulphuric acid. The solubility in acids may be restored by fusion with caustic potash or with nitrate of potash. In this it much resembles zirconia and titanic acid.—Ed.

[2] If oxyde of chromium and its compounds be fused with nitrate of potash, it is converted into chromic acid which combining with the potash of the nitrate forms chromate of potash, the aqueous solution of which is yellow.—Ed.

or of ammonia with sulphate of chromium (potassio-sulphate of chromium). These purple salts produce with water, in the cold, a purple solution, in which crystals are formed when the liquor is abandoned to spontaneous evaporation.

* If, on the contrary, the violet aqueous solution be boiled, or even if submitted to a more gentle heat, the liquid becomes emerald-green, and the salt will no longer crystallise by spontaneous evaporation. The solution of the corresponding chloride of chromium is emerald green; even after having been submitted to a heat which is not higher than that of boiling water, the solution of chloride of chromium retains that colour; but, if it be heated a little beyond that temperature, it becomes of a peach-blossom red colour, but the primitive colour may be restored by merely adding water.

The solutions of oxyde of chromium in acids, and that of salts of chromium in water behave towards re-agents in the following manner:—

A small quantity of solution of POTASH produces a light-green precipitate of hydrate of deutoxyde of chromium, which, in the cold, dissolves easily and completely in an excess of the re-agent. The colour of such solutions is green, having ordinarily the same appearance as before the addition of the potash. When this solution is boiled [for a long time] the whole of the oxyde of chromium is precipitated; it has a green colour, and the supernatant liquid is as limpid as water. This precipitate appears also green by artificial light.

AMMONIA determines in solutions of oxyde of chromium a bluish-grey precipitate of hydrate of oxyde of chromium, which has a tinge of violet. This precipitate appears entirely of a violet colour by artificial light. The supernatant liquid is reddish, and contains as yet some trace of oxyde of chromium which may be precipitated therefrom by a prolonged digestion, and likewise by boiling[1].

A solution of CARBONATE OF POTASH forms in solutions of oxyde of chromium a light green precipitate of hydrate of oxyde of chromium, * which contains a little carbonic acid. This precipitate becomes almost blue by long standing, and viewed by artificial light it appears violet. A small quantity of it is dissolved by the re-agent, so that the supernatant liquor is green, and after a longer time it appears bluish. The precipitated oxyde is completely soluble in a very large excess of the re-agent, and there is no precipitate by ebullition from this solution.

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[1] Dr. Fresenius observes, that if, an excess of ammonia being added, the mixture be heated, the whole of the hydrated oxyde of chromium will be precipitated.—ED.

A solution of BICARBONATE OF POTASH produces a precipitate of a light green colour, which has the same composition as that produced by carbonate of potash, and the supernatant liquid is greenish. By long standing both this precipitate and supernatant liquid become bluish. The precipitate appears violet by artificial light.

A solution of CARBONATE OF AMMONIA behaves in the same manner.

A solution of PHOSPHATE OF SODA produces a light green precipitate of phosphate of oxyde of chromium in neutral solutions of oxyde of chromium.

A solution of OXALIC ACID, nothing.

A solution of FERROCYANURET OF POTASSIUM, nothing.

A solution of FERRICYANURET OF POTASSIUM, nothing.

A solution of CHROMATE OF POTASH imparts a yellowish-brown colour to an acid solution of oxyde of chromium; if ammonia be added, a yellowish-brown precipitate of chromate of oxyde of chromium is subsequently formed, and the supernatant liquid retains a yellowish-brown colour. A solution of chromate of potash poured in a neutral solution of oxyde of chromium determines an immediate yellow precipitate of chromate of oxyde of chromium, and the supernatant liquor has a yellowish-brown colour.

A solution of IODIDE OF POTASSIUM produces in neutral solutions of oxyde of chromium a light green precipitate of iodide of chromium, soluble in muriatic acid.

HYDROSULPHURET OF AMMONIA produces in a neutral solution of oxyde of chromium a greenish precipitate of oxyde of chromium, * probably mixed with a little sulphuret of chromium.

A solution, or a current of SULPHURETTED HYDROGEN GAS does not determine any precipitate in acid or in neutral solutions of oxyde of chromium.

The neutral salts of oxyde of chromium, which are soluble in water, redden litmus paper.

The salts of oxyde of chromium,which are soluble in water, are decomposed by exposure to a red heat.

Most of the salts of oxyde of chromium which are insoluble in water, are soluble in acids; when they have not been ignited their acid solutions behave very often like the acid solutions of pure oxyde of chromium, so that in many cases there is a risk of overlooking the acid with which the oxyde of chromium forms the compounds which are insoluble in water. By having recourse to the blow-pipe, however, the presence of oxyde of chromium may soon be detected in these combinations.

Before the BLOW-PIPE, oxyde of chromium and its combinations are most easily recognised by the fine emerald-green colour which they communicate to fluxes. The colour of the fluxes is equally green in the interior and in the exterior flames, at least such is the case with microcosmic salt; by this character may oxyde of chromium be distinguished from protoxyde of copper [which produces a green bead only in the exterior flame].

* Most of the compounds of oxyde of chromium in the dry state, are easily recognised by means of the blow-pipe, even when there is only the slightest trace of this oxyde, and may be distinguished from the greatest part of the combinations which have hitherto been treated of. The solutions of the compounds of oxyde of chromium may be recognised by their colour. They may also be distinguished from the green solutions of other substances, because the solution of sulphuretted hydrogen does not produce any precipitate, and in general does not produce any change in them.

* Oxyde of chromium has much resemblance to protoxyde of

uranium, not only as regards the colour of its solutions, but also by its behaviour towards the blow-pipe; the solution of protoxyde of uranium, however, turns yellow when treated by nitric acid, which oxydises it; and by the action of which it is converted partly into uranic acid. It differs also from a solution of oxyde of chromium by its behaviour towards the solutions of oxalic acid, of ferrocyanuret of potassium, and of hydrosulphuret of ammonia[1].

The presence of non-volatile organic substances does not prevent the precipitation of oxyde of chromium by alkalies.

* When we treat of the acids, the highest degree of oxydisation of chromium, namely chromic acid, will be examined.

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[1] By referring to the behaviour of potash and of ammonia, it will be seen that the precipitate produced by the first of these tests in solutions of oxyde of chrome, is easily dissolved by an excess of the re-agent, and that the second precipitates oxyde of chromium from these solutions; characters which belong also to alumina, which is likewise dissolved by an excess of potash, and precipitated altogether by ammonia; hence the possibility of overlooking the presence of alumina in the precipitates of oxyde of chromium. But by mixing the precipitated oxyde of chromium with an excess of carbonate and of nitrate of potash, and keeping it fused for some time, the oxyde of chromium becomes converted into chromate of potash, which is soluble in water, whilst the alumina remains undissolved. Or, for qualitative analysis, the precipitated oxyde of chromium may simply be mixed with a large excess of carbonate of potash, which will dissolve it, whilst alumina is almost insoluble in this re-agent; or else the precipitated oxyde of chromium may be *boiled* with an excess of potash, which will altogether precipitate it, whilst the alumina will remain in solution.—Ed.

SECTION II.

ACIDS.

CHAPTER I.—OXACIDS.

1. ACIDS OF SULPHUR.

1°. SULPHURIC ACID, SO_3.

(*Acide Sulphurique.*)

Pure anhydrous sulphuric acid is a crystalline, tough mass, resembling asbestus, and which emits very thick white fumes in the air. It is quite clear that this dry acid can be but very seldom met with for analysis. Aqueous sulphuric acid is sometimes fuming, (*Nordhausen,* or fuming oil of vitriol), in which case, if the temperature is somewhat lowered, it very easily deposits crystals; at other times, and it is under this form that it is most often met with, it is not fuming, but has an oily consistency. English oil of vitriol in the pure state, both the fuming and non-fuming sulphuric acid, are colourless; the former, however, has often a brownish colour, which is created by a very small quantity of organic matter. This acid boils at a much higher temperature than water, and is not decomposed by ebullition. It has a violent destructive action upon organic substances, and absorbs the moisture of the air; when it is mixed with alcohol or with water much heat is developed.

With the bases sulphuric acid forms salts, which are called *sulphates,* amongst which the supersulphates and the neutral sulphates are all soluble in water, with the exception of the combinations which this acid forms with baryta, strontia, oxyde of lead, and lime, which are insoluble or very sparingly soluble in water, and which do not dissolve either in an excess of the dilute acids. Almost all the basic sulphates are insoluble in water, but dissolve in the dilute acids. The neutral sulphates are insoluble in strong alcohol, excepting the combinations of sulphuric acid with peroxyde of iron, oxyde of chromium, and a small number of other bases which contain a large number of atoms of oxygen.

* For the purpose of detecting the smallest possible quantity of free sulphuric acid, and of distinguishing it, in a liquid, from that which being combined with bases forms soluble salts with them, Runge uses a solution of cane sugar. Sulphuric acid in effect decomposes sugar at a temperature of 100° cent.[1], producing at the same time peculiar changes of colour, which vary according to the quantity of sugar put in contact with it. When a piece of china is coated with a solution of 1 part of sugar in 30 of water, one small drop of a liquid containing 1 part of sulphuric acid in 300 of water placed upon it, and heated by steam, is sufficient to form a spot of an intense black colour. If the proportion of water be more considerable, the colour changes, and becomes greenish when upon the heated surface of solution of sugar one drop of liquor is let fall which contains no more than 1 part of sulphuric acid in 8000 of water.

* The solutions of the neutral sulphates, and of the sulphates which redden litmus paper, do not produce this reaction, which consequently is an excellent one for the detection of sulphuric acid *in a free state* from that of sulphuric acid in a state of combination.

* Neither phosphoric acid nor other acids can thus decompose sugar, and therefore their presence is no impediment to the use of the test.

The presence of either free or combined sulphuric acid is most easily detected in salts which are soluble in water, because, even in very dilute solutions, the addition of the solution of a barytic salt produces a white precipitate of sulphate of baryta, which is not dissolved by the further addition of a free acid. The barytic salt which is generally employed, and in the greatest number of cases the most suitable for the purpose, is chloride of barium; and muriatic acid is the acid generally preferred for the addition of a free acid just alluded to. When muriatic or nitric acid has been poured in the solution of the salt under examination, it should be observed that if a *concentrated* solution of chloride of barium or of nitrate of baryta be then added, a white precipitate of chloride of barium or of nitrate of baryta may be produced, because these salts are much less soluble in free acids than in water; but the addition of water completely dissolves such precipitates.

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[1] 212° Fahrenheit.—Ed.

* When an acid liquor is not rendered turbid immediately, but only after a time, by solution of a barytic salt, it is certainly a proof that it contains sulphuric acid; but that quantity is very small, almost imponderable; and as, with the exception of selenic acid, no other acid beside sulphuric acid forms with baryta a compound which is completely insoluble in water and in dilute acids, it is very easy by means of the solution of a barytic salt to recognise sulphuric acid in solutions, and to distinguish it from other acids[1].

Solutions of PROTOSALTS OF LEAD likewise determine, in solutions of sulphuric acid, or of the sulphates, a white precipitate of sulphate of lead, which differs from the analogous white precipitates which contain protoxyde of lead, because it is insoluble in dilute nitric acid[1]. It is, however, far less easy with solutions of protosalts of lead than with those of the barytic salts to detect very minute quantites of sulphates dissolved in a liquid.

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[1] Salts of baryta produce also in solutions of selenic acid a white precipitate, which is seleniate of baryta, which is insoluble in nitric acid, but soluble in boiling muriatic acid under disengagement of chlorine, a circumstance which distinguishes it from sulphate of baryta. The seleniate is thereby converted into a selenite. Hydrofluosilicic acid is another acid which produces also, with salts of baryta, a white precipitate, which being almost insoluble in both nitric and in muriatic acids, might be mistaken for sulphate of baryta, from which however it may be distinguished by testing the solution which produced it with a salt of lead or of strontia, with which hydrofluosilicic acid forms no precipitate; and likewise because the precipitate of hydrofluosilicic acid and baryta does not evolve the odour of sulphurous acid when heated by the blow-pipe, as described further on.—ED.

The aqueous solution of sulphuric acid and of the sulphates are not disturbed by solution of SULPHURETTED HYDROGEN, provided the acid be not combined with a base susceptible of being precipitated by this re-agent.

The presence of sulphuric acid in the basic sulphates, which are insoluble in water, may be detected by first dissolving them in dilute muriatic acid, and then water being added to the liquor, chloride of barium is to be poured in, which precipitates the sulphuric acid in the state of insoluble sulphate of baryta.

But in order to detect the presence of sulphuric acid in the sulphates which are insoluble, or very sparingly soluble, in water and in acids,—for example, in sulphate of baryta, of strontia, of lead, and of lime,—it is necessary to boil these salts with a solution of carbonate of potash or of soda; the liquor is then to be filtered, in order to separate the insoluble portion, and this filtered liquor is to be super-saturated with muriatic acid, and a solution of chloride of barium being now poured in, it will produce a white precipitate of sulphate of baryta, if the insoluble compound contained sulphuric acid[2].

The neutral sulphates, when their base is an alkali, or baryta, strontia, lime, protoxyde of lead, or magnesia, are not decomposed by heat. Those the base of which is protoxyde of manganese, protoxyde of zinc, oxyde of cobalt, oxyde of nickel, oxyde of cadmium, and protoxyde of copper, are decomposable by a very strong heat; the decomposition, however, is often incomplete, at least when the quantity of salt is large. The combinations which sulphuric acid forms with alumina, sesquioxyde of iron, and even with protoxyde of iron and protoxyde of tin, are more easily decomposed when heated in contact with the air, and ultimately leave pure oxydes after having been strongly heated. The combination of sulphuric acid with oxyde of silver leaves pure silver after exposure to a red heat; that of sulphuric acid with suboxyde or with protoxyde of mercury leaves no residuum.

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[1] But it is pretty soluble in hot concentrated muriatic acid, on cooling the liquor deposits crystals of chloride of lead.—ED.

[2] The insoluble sulphate is converted by this treatment into sulphate of soda, which is soluble, and into an insoluble carbonate of the base which remains on the filter. Fusion with the alkaline carbonates produces the same effect, that is to say, by digesting the fused mass with water and filtering, the soluble alkaline sulphate will be found in the filtered liquid, and an insoluble carbonate of the base will be left on the filter. With sulphate of lead, however, that which is left on the filter is pure oxyde of lead, not carbonate of lead.—ED.

The solutions of the neutral combinations of sulphuric acid with the alkalies, with lime, magnesia, protoxyde of manganese, and oxyde of silver, do not alter the colour of blue litmus paper. The neutral combinations of that acid with other bases redden litmus paper.

The presence of sulphuric acid in sulphates, especially those the base of which is not, properly speaking, a metallic oxyde, whether soluble or insoluble, are recognised with the BLOW-PIPE in the following manner:—A small portion of the salt is to be put upon a clear and colourless bead, obtained by fusing a mixture of soda and silica upon charcoal, the whole being heated in the interior flame; the bead becomes dark brown, or if the sulphuric acid was in a small quantity, the colour becomes red on cooling. A little of the sulphate may also be heated with soda upon charcoal in the interior of the flame, and the fused mass is to be deposited upon a piece of bright silver; if it be now moistened, the piece of silver becomes black, or dark yellow, at the point where it was in contact with the mass in question[1].

When the base of the sulphates is a metallic oxyde, the presence of sulphuric acid may be detected therein, in most cases, by means of the blow-pipe; for they then emit the smell of sulphurous acid gas when they are brought to a red heat upon charcoal. But a more accurate method consists in putting a small quantity of the salt upon charcoal, and heating it to redness, in order to dissipate the water of crystallisation; it is then to be pulverised in a small mortar, and mixed with a small quantity of charcoal in powder; the mixture being now heated by the blow-pipe in a small glass tube closed at one end, there is a large disengagement of sulphurous acid, which is soon recognised as such by its odour, and by the property it has of bleaching a strip of moist brazil-wood paper introduced in the upper part of the tube.

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[1] This discolouring is owing to the formation of sulphuret of silver.—ED.

The combinations of sulphuric acid with the alkalies and the earths do not evolve the smell of sulphurous acid when thus treated by charcoal.

The behaviour of sulphuric acid and of the sulphates towards a solution of baryta is perfectly characteristic, and prevents the possibility of confounding this acid with any other, except selenic acid, of which we shall speak hereafter.

* Concentrated (English) sulphuric acid dissolves at the ordinary temperature a great number of non-volatile and volatile organic substances, and when care is taken to avoid as much as possible heating the solution, this solution forms after dilution with water a liquor which sometimes is colourless, and which at other times is more or less brown. In such solutions one part of sulphuric acid is combined with the organic substance, in conjunction with which baryta, strontia, lime, and protoxyde of lead form salts, which most frequently are soluble or more rarely are sparingly soluble or altogether insoluble in water, in consequence of which it is impossible by means of chloride of barium to determine the formation of a precipitate in solutions of the salts which sulphuric acid, combined with the organic substances, forms with the other bases. When, however, an organic substance has been treated by sulphuric acid, as we have just said, the whole of the acid is never combined with it; portions of it are always left in a free state, and if the whole be diluted with water, the solution will consequently always afford a precipitate of sulphate of baryta when tested by chloride of barium.

2°. HYPOSULPHURIC ACID, S_2O_5.

(Acide Hyposulphurique.)

* HYPOSULPHURIC ACID in the pure state and in aqueous solutions is of rare occurrence in analytical chemistry. In this state it is inodorous, and has a powerfully acid reaction. When an attempt is made to concentrate it much by evaporation, it is decomposed, sulphurous acid gas is disengaged, and sulphuric acid remains. Hyposulphuric acid forms soluble salts with all the bases, owing to which the aqueous solution of the acid or of its salts is not precipitated by solutions of baryta, strontia, lime, and protoxyde of lead. If a precipitate is formed, it is a proof that the liquid contains sulphuric acid also.

* The aqueous solutions of hyposulphuric acid have the same deportment as that of its salts. The latter may be easily identified in the following manner.

* When MURIATIC ACID is poured in the solution of a hyposulphate, no change is produced in the cold; but if the mixture be then boiled a decomposition takes place, there is a perceptible odour of sulphurous acid emitted, and the liquid then contains sulphuric acid, the presence of which may be rendered manifest by solution of a barytic salt. In this operation there is not the slightest deposition of sulphur. If hyposulphuric acid was combined in the solution with baryta, strontia, protoxyde of lead or lime, boiling it with muriatic acid causes an insoluble or very sparingly soluble precipitate, which is due to a combination of sulphuric acid with these bases.

* The change produced by muriatic acid is more easily obtained still by sulphuric acid, which, in the cold, produces no reaction, except that it at once forms an insoluble precipitate when the hyposulphuric acid is combined with a base with which sulphuric acid forms an insoluble salt; but when the mixture is heated, a very distinct smell of sulphurous acid is evolved, which, in such a case, is more perceptible when muriatic acid has been employed.

* When dilute SULPHURIC ACID is added to a solution of green manganate of potash (mineral cameleon) which imparts a

deep red colour to the liquor, if some solution of a hyposulphate be now added, the red colour does not undergo any change in the cold; but as soon as the mixture is boiled the liquid becomes discoloured, because sulphurous acid is then disengaged.

* When MURIATIC ACID is added, in the cold, to the solution of a hyposulphate, and if a solution of SULPHURETTED HYDROGEN GAS be next added to the liquor, no sulphur is separated, even after a long time, provided the operation be made out of contact with the air; but if the solution of hyposulphate has at all been boiled with muriatic acid, the addition of sulphuretted hydrogen produces at once a considerable milkiness, which is owing to a liberation of sulphur, because sulphuric acid is then present in the liquor.

* When muriatic acid has been poured, in the cold, in the solution of a hyposulphate, if a solution of an easily reducible metal be then added, for example, solution of perchloride of gold, no metal is precipitated in the cold, but, by boiling, the metal is precipitated, because sulphurous acid is then formed, which effects the reduction.

* When the solution of a hyposulphate is treated, in the cold, by NITRIC ACID, no change is produced; but as soon as the whole is boiled, yellow fumes of nitrous acid are disengaged, the hyposulphuric acid is converted into sulphuric acid, and in fact there is a production of the latter acid in a quantity which is double that which is required to saturate the base with which the hyposulphuric acid was combined. Wherefore, when solution of hyposulphate of baryta is boiled with nitric acid, insoluble sulphate of baryta is formed, and the liquor filtered from this precipitate is found to contain free sulphuric acid.

* If nitric acid be added to a solution of the green MANGANATE OF POTASH, by which it is rendered intensely red, and if a solution of a hyposulphate be then further added, the red colour remains unaltered not only in the cold way but also when boiled, because the sulphurous acid liberated is converted into sulphuric acid.

* When a current of GASEOUS CHLORINE is passed through the solution of a hyposulphate, the hyposulphuric acid is not

converted into sulphuric acid; but if the solution being saturated with chlorine is then boiled this conversion is effected.

* Hyposulphates in the solid state are easily recognised, because it is sufficient to heat even a very small quantity in a glass tube blown into a bulb at one end, and over a spirit lamp, in order to perceive the smell of the sulphurous acid which is evolved. There remains in the tube a neutral sulphate, provided it has been heated long enough. Hyposulphates are not blackened by heat.

* When a hyposulphate is projected in NITRATE OF POTASH in the state of fusion, ruddy fumes of nitrous acid are evolved, and the hyposulphate is converted into a sulphate.

* Before the BLOW-PIPE, hyposulphates have the same reaction as the sulphates, when fused with a globule of soda and silica; their comportment with a piece of silver upon which they are deposited after fusion with soda upon charcoal is also the same (page 204.)

* Hyposulphates may be recognised in solutions, because, when heated with acids, they are converted into sulphates and into sulphurous acid. In the solid form they are well and easily identified by the effect of heat upon them.

3°. SULPHUROUS ACID, SO_2.

(*Acide Sulphureux*).

PURE sulphurous acid is a gas which has a peculiar suffocating odour by which the smallest quantities may readily be detected[1]. Submitted to an intense cold and strong pressure it may be obtained in the form of a limpid liquid[2]. The gas discolours moist brazil-wood paper.

Sulphurous acid gas is soluble in water, but is more soluble still in alcohol[3]. These solutions have the characteristic suffocating odour of the gas; they have also a peculiar taste, and discolour Brazil wood paper. By long exposure to the air the sulphurous acid which they contain gradually absorbs oxygen, and it becomes partially or entirely converted into sulphuric acid.

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[1] This odour is that which is produced by burning sulphur.—ED.

[2] According to Professor Faraday, the pressure required for the liquefaction of sulphurous acid gas is two atmospheres; but M. Bussy obtained it in the liquid form at the ordinary atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of salt and snow.—ED.

[3] According to M. Graham, recently boiled water at mean temperature and

The solutions of SULPHUROUS ACID lose their odour by prolonged ebullition, because the acid is thereby volatilised. They lose it also when digested with peroxyde of lead (brown oxyde of lead) because the excess of the oxygen of the base causes the acid to pass to a higher degree of acidification, and the result is sulphate of protoxyde of lead.

The solutions of the soluble sulphites do not exhale the odour of sulphurous acid when they are neutral, but they have the peculiar taste of this acid even when the salt contains an excess of base. They are recognized by the odour of sulphurous acid, which they evolve when they are mixed with muriatic acid, or still better, with sulphuric acid; in the latter case, the sulphurous acid smell is very distinct. If the solution of the sulphite be very concentrated, sulphurous acid is disengaged with effervescence at the moment when the acid is poured in: the remaining liquor does not contain any sulphuric acid when the decomposition has been effected by muriatic acid: no sulphur is deposited during this decomposition. When nitric acid is poured, in the cold, in the concentrated solution of a sulphite, sulphurous acid is disengaged; but if the whole be boiled, there is a disengagement of ruddy fumes of nitrous acid, and formation of sulphuric acid.

Sulphurous acid is detected in solutions by adding SULPHURETTED HYDROGEN thereto, by which a milky white precipitate of sulphur is determined. If the liquor contain a sulphite the precipitate of sulphur does not appear, unless, before pouring the solution of sulphuretted hydrogen, muriatic acid or dilute sulphuric acid has been added.

* When to a solution of green manganate of potash a little sulphuric acid is added, and by which it is strongly reddened,

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pressure dissolves 37 volumes of sulphurous acid gas, but one volume of alcohol takes up more than 100 volumes of the gas.—ED.

the solution of a sulphite, or an aqueous solution of sulphurous acid, is further poured in, the red colour is instantly dissipated[1].

When solutions of sulphites are mixed with those of certain metallic salts, and a strong acid—for example, muriatic acid, or dilute sulphuric acid—is further added, the metals are reduced. From a solution of perchloride of gold, gold is reduced even in the cold. If the solutions of a sulphite be mixed with a solution of nitrate of silver, at first a white precipitate of sulphite of silver may be determined, * which is very soluble in an excess of the sulphite, and which in course of time, but more rapidly by boiling, is easily converted into metallic silver, which very often coats the sides of the vessels with a bright silvery film.

When the solution of a protosalt of copper is boiled with that of alkaline sulphites, the protoxyde of copper is reduced in the state of suboxyde, which combines with the sulphurous acid, and produces a voluminous light-brown precipitate, which is decomposed by an addition of dilute sulphuric acid. A solution of telluric acid in muriatic acid, treated in the same way, gives a pulverulent black precipitate of metallic tellurium; and a solution of selenious acid gives a cinnabar-red precipitate, which remains a long time in suspension, and is metallic selenium: the latter precipitate is reduced to a very small bulk, and assumes a black colour by boiling.

* The presence of very small quantities of sulphurous acid and of sulphites may be recognized by adding to the solution of these bodies a solution of PROTOCHLORIDE OF TIN in muriatic acid, or else first adding muriatic acid, and then some pure crystals of protochloride of tin. After some time, either the liquor turns brown, and subsequently deposits a brown precipitate, which consists principally of sulphuret of tin; or else, if whole crystals of protochloride of tin have been employed, the crystals are surrounded by the brown deposit. The same

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[1] When *iodic acid* is mixed with sulphurous acid, the iodic acid is decomposed by the deoxydating influence of sulphurous acid, and free iodine may then be detected in the liquor by adding solution of starch, which, in the cold, forms a blue compound of iodine and starch.—ED.

phenomenon often occurs when pure crystals of protochloride of tin are dissolved in muriatic acid; but this takes place only when the muriatic acid employed contains traces of sulphurous acid, the presence of which cannot often be detected, according to Girardin, in any other way[1].

Sulphurous acid forms soluble salts with alkalies. Its compounds with the earths are insoluble in water, but soluble in acids. This is why a solution of *chloride of barium* produces, in neutral solutions of sulphites, a white precipitate of sulphite of baryta, which is completely soluble in dilute muriatic acid. But when the solution of the sulphite has been left exposed to the air for a long time, the oxygen of the air being absorbed forms sulphuric acid, and the precipitate produced by chloride of barium is no longer completely soluble in muriatic acid[2].

A solution of CHLORIDE OF CALCIUM likewise produces a precipitate soluble in muriatic acid.

A solution of a PROTOSALT OF LEAD produces a precipitate of sulphite of lead, which is completely soluble in cold nitric acid, but, by boiling, yellow fumes of nitrous acid are disengaged, and insoluble sulphate of lead is produced.

In the solid form, sulphites are recognized by the odour of sulphurous acid which they evolve when an acid is poured upon them, and because, when heated to redness in a tube blown into a bulb at one end, they at first begin to fuse, and are then converted into a metallic sulphuret and a sulphate. When a dilute acid is poured upon the mass which has been exposed to a red heat, sulphuretted hydrogen is disengaged, provided the metallic sulphuret is one which can decompose water under the influence of the dilute acid, and consequently thus give rise to a disengagement of sulphuretted hydrogen.

* When a portion of sulphite is projected upon nitrate of potash in a state of fusion, there is a disengagement of ruddy

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[1] Messrs. Fordos and Gélis have indicated a better method than that by protochloride of tin to detect traces of sulphurous acid in muriatic acid. I have described this method in the second part.—Ed.

[2] The insoluble portion being sulphate of baryta.—Ed.

fumes of nitrous acid, and the sulphite is converted into sulphate.

Before the BLOW-PIPE, the sulphites behave in the same manner as the sulphates, when treated with a globule of soda and silica, and when, after fusion upon charcoal with soda, they are thrown upon a piece of silver.

The sulphites may easily be recognized by the characteristic odour of sulphurous acid, which they emit when treated by muriatic acid or by dilute sulphuric acid, which evolution is not accompanied by separation of sulphur.

* They may also be recognized because they evolve an odour of sulphurous acid when heated with muriatic acid, no sulphuric acid being thereby formed, which character distinguishes them from hyposulphates. They may also be very well distinguished from the latter salts by the behaviour of their solutions towards those of chloride of barium, of calcium, and of protosalts of lead; and also by the manner in which the sulphites in the solid form behave when exposed to a high temperature. In a word, the properties which have just been detailed establish such a marked distinction as almost to preclude the possibility of confounding them with other salts.

The French edition has the following addition by Mons. E. Peligot:—

* Two new compounds of sulphur and oxygen have been lately discovered, so that we now know of six combinations formed by these two bodies.

SULPHYPOSULPHURIC ACID, S_3O_5.

(Acide Sulfhyposulfurique.)

* M. LANGLOIS discovered this new acid; it is a compound of three equivalents of sulphur with five of oxygen, and he obtained it in combination with potash by digesting for several days well levigated flowers of sulphur in a solution of bisulphate of

potash. The temperature to which the mixture is submitted must not be above 60° cent. (140° Fahr.)

* Sulphyposulphate of potash crystallises in four-sided prisms, terminated by dihedral summits, unalterable in the air. It has a bitter saline taste, is very soluble in water, and insoluble in alcohol. It is decomposed by heat, and thereby transformed into sulphate of potash under disengagement of sulphurous acid gas and deposition of sulphur. It is decomposed both by nitric and by sulphuric acid; muriatic, chloric, and iodic acids have no action upon it; but by treatment with perchloric acid, the sulphyposulphuric acid is easily isolated[1].

* Pure sulphyposulphate of potash, in the cold, causes no precipitate in solutions of salts of calcium, of barium, or of lead. It discolours the red solution of sulphate of manganese, but has no action upon the solution of sulphate of copper. It precipitates sulphuret of mercury from the salts of suboxyde of mercury, and sulphate [sulphate of suboxyde] of mercury from the salts [salts of protoxyde] of that metal[2]. It produces in solution of nitrate of silver a yellowish-white precipitate, which soon turns black[3].

* Sulphyposulphuric acid is liquid, colourless, of a slightly astringent and bitter taste. It cannot be obtained entirely pure, except immediately after its separation from potash; concentrated in vacuo, it gradually undergoes decomposition, forming sulphur, sulphurous, and sulphuric acids[4]. With the help of heat this decomposition takes place very rapidly, and also by treatment with other acids, even those which do not act upon sulphyposulphate of potash.

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[1] The perchloric acid must be cautiously added so long as a precipitate of perchlorate of potash is formed. The clear liquor is to be decanted and evaporated in vacuo over concentrated sulphuric acid.—Ed.

[2] That is to say, if poured in solution of subnitrate of mercury, sulphuret of mercury is precipitated, and in solution of protochloride of mercury (corrosive sublimate) sulphate of mercury is thrown down.—Ed.

[3] Sulphyposulphates produce no precipitate in solutions of barium, strontium, magnesium, aluminum, lead, iron, zinc, nickel, cobalt, uranium, &c., &c.—Ed.

[4] This decomposition, according to M. Langlois, takes place spontaneously also, but by no means rapidly, for after eighteen months he found most of the acid as yet undecomposed.—Ed.

BISULPHYPOSULPHURIC ACID, S_4O_5;

OR,

BISULPHURETTED HYPOSULPHURIC ACID.

(Acide Bisulfhyposulfurique);

or,

(Acide Hyposulfurique Bisulfuré.)

* THIS acid was discovered by Messrs. Fordos and Gélis, and it is produced whenever an aqueous solution of hyposulphite is placed in contact with iodine; two equivalents of hyposulphite are decomposed by one of iodine; the result is a metallic iodide, and the equivalent of oxygen, which was united to the metal, combines with the four equivalents of oxygen of the hyposulphurous acid to form the new acid.

* Hyposulphite of baryta is the most appropriate salt for the preparation of bisulphuretted hyposulphuric acid. This salt is to be held suspended in water, and iodine is added until the mixture begins to change colour, and when the iodine and hyposulphite have dissolved, the new salt which is then formed is gradually deposited, and ultimately the liquor thickens to a mass, which is to be treated by alcohol to separate the free iodine and the iodide of barium[1].

* By treating the bisulphuretted hyposulphate thus obtained with the quantity of dilute sulphuric acid strictly necessary to precipitate the base, the acid is liberated, and may be separated from the sulphate of baryta formed by filtering[2].

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[1] Hyposulphite of barium may be prepared by precipitating a concentrated solution of hyposulphite of soda by a concentrated solution of acetate of baryta, and washing the precipitate with dilute alcohol to remove the acetate of soda. This precipitate is then to be mixed with water to a creamy consistence, and iodine added in successive small portions; the mass dissolves rapidly, owing to the formation of iodide of barium, and of the salt of the new acid, which is also soluble in water; but the quantity of the new salt formed becoming more and more considerable, it deposits in flakes at first, but lastly the whole forms a thick mass. Concentrated alcohol is now to be added, which dissolves the iodide of barium and the excess of iodine, and leaves the new barytic salt under the form of a white crystalline powder, which is to be well washed with alcohol and dried. From this salt the new acid may be obtained as described.—ED.

[2] Bisulphuretted hyposulphate of baryta contains two atoms of water. It may be represented by $BaO + S_4O_5 + 2$ aq.; therefore the atomic weight is 199·24,

* **Bisulphuretted hyposulphuric acid** is colourless, inodorous, with a decided acid taste. It may be concentrated to a great extent without undergoing decomposition; yet it is unstable, and even at the ordinary temperature its elements gradually separate, forming sulphur, sulphurous, and sulphuric acids.

* It is not altered by dilute muriatic or sulphuric acids. Nitric acid, on the contrary, has a powerful action upon it, and precipitates sulphur.

* It forms a white precipitate in solution of protochloride of tin and in protochloride of mercury (sublimate), a yellow precipitate in solution of subnitrate of mercury; but if there be an excess of salt, the precipitate is black. With nitrate of silver the precipitate is at first white, but in a few moments it becomes yellow, and then black.—E. Peligot.

4°. HYPOSULPHUROUS ACID, S_2O_2.

(*Acide Hyposulfureux.*)

* In the pure state, or even in combination with water, this acid may be said to be as yet unknown, because, in all attempts made towards separating it from its bases, by treating any of its salts by a stronger acid, it is soon decomposed.

* Its combinations with most bases are soluble in water, yet hyposulphite of baryta is very sparingly so, owing to which, when chloride of barium is poured in a solution of a very soluble hyposulphite, provided such a solution be not too dilute, a precipitate of hyposulphite of baryta is formed, which, however, may be completely dissolved by a large quantity of water.

* Hyposulphurous acid in solutions of the hyposulphites may be detected in various ways.

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which weight must be mixed with one atomic weight of hydrated sulphuric acid previously diluted with four times its weight of water and suffered to cool, small portions only of which must be added at a time, to prevent too great an elevation of temperature, which might decompose the acid. The liquid is then filtered to separate the sulphate of baryta, and evaporated in vacuo over sulphuric acid.—Ed.

* When MURIATIC ACID is poured in these solutions, a milkiness is produced after a time, which is owing to a liberation of sulphur, and which increases, whilst at the same time an odour of sulphurous acid is evolved. If the solution of the hyposulphite is not very dilute, the precipitated sulphur has a yellow colour, even when the decomposition by muriatic acid is effected in the cold. The decomposition of hyposulphites into sulphur, which precipitates, and sulphurous acid, which is disengaged, takes place slowly, and is not yet complete after some weeks, even though the mixture be kept continually warm, provided the quantity of salt is not too small; for if, after this lapse of time, an excess of nitrate of silver is poured in the solution decomposed by muriatic acid, a white precipitate of chloride of silver is at first formed, it is true; but after a time, more or less considerable, this precipitate becomes brown or black, because sulphuret of silver is produced.

* Other acids react upon the hyposulphites in the same way as muriatic acid. Nitric acid, in the cold, produces the same changes; but by boiling the liquor, it oxydises the hyposulphurous acid, which becomes converted into sulphuric acid, and sulphur is precipitated. If the whole of the hyposulphurous acid be converted into sulphuric acid, its oxydisation is found to have produced double the quantity of the acid which is required to saturate the base with which it was combined in the state of a neutral salt.

* A solution of NITRATE OF SILVER produces in the solution of a hyposulphite a precipitate, which at the beginning is white, and which consists of a hyposulphite of silver; but it soon becomes yellowish-brown, and ultimately black, which changes especially take place with rapidity when the whole is boiled. The black precipitate is sulphuret of silver. The liquid filtered from this precipitate contains half the sulphur of the hyposulphite in the state of sulphuric acid; wherefore a solution of nitrate of baryta produces therein an abundant precipitate of sulphate of baryta. These phenomena take place both when there is an excess of either solution of silver, or of solution of hyposulphite. When to a solution of nitrate of silver, one of

chloride of sodium or of potassium is added, the chloride of silver, which is thereby produced, is completely dissolved by the solution of a hyposulphite, and neither time nor ebullition can produce black sulphuret of silver in such a solution.

* A solution of SALT OF PROTOXYDE OF MERCURY, or of PROTOCHLORIDE OF MERCURY (sublimate), poured in large quantity in that of a hyposulphite, produces a white precipitate, which remains long suspended in the liquor, and which is not discoloured by either time or ebullition. This precipitate is a combination of sulphuret of mercury with the protosalt of mercury, or the protochloride of mercury, which has been employed. The liquor filtered therefrom contains sulphuric acid, and gives consequently an abundant precipitate of sulphate of baryta, by addition of chloride of barium. If, on the contrary, a large excess of solution of the hyposulphite be poured in the solution of salt of protoxyde, or of protochloride of mercury, the precipitate which is at first produced is white, but it very soon becomes yellowish-brown, and lastly, black, which changes are much accelerated by boiling the whole. The black precipitate is sulphuret of mercury, and the supernatant liquid contains sulphuric acid.

* A solution of SUBNITRATE OF MERCURY produces, in solution of a hyposulphite, an immediate black precipitate of sulphuret of mercury, no matter which solution is in excess, that of the hyposulphite, or of the subnitrate.

* A solution of a SALT OF PROTOXYDE OF COPPER, or of PROTOCHLORIDE OF COPPER, does not produce any precipitate in solutions of hyposulphites. Yet, in course of time, a turbidness of a brown colour appears, and some subchloride of copper separates from the solution of protochloride of copper. If, on the contrary, the mixture be boiled, a black precipitate of sulphuret of copper is very rapidly formed. The supernatant liquid contains sulphuric acid.

* If to the solution of a very small quantity of hyposulphite a solution of PROTOCHLORIDE OF TIN in muriatic acid be added, a brown precipitate is formed, after a time, which is analogous to that produced in similar circumstances by sulphurous acid,

or by a sulphite (page 210), the only difference being, that in the present instance the formation of the precipitate takes place more rapidly. By this test traces, too minute to be otherwise detected by the other re-agents, become manifest.

* Most solutions of hyposulphites are not altered by boiling. Hyposulphite of lime must, however, be excepted, for it is thereby decomposed into sulphite of lime and sulphur.

* When muriatic acid is let fall drop by drop upon the hyposulphites in the solid state, sulphurous acid gas is disengaged with effervescence, which may be easily recognized as such by the smell, even though a very small quantity of hyposulphite be treated. If the salt is placed upon a piece of silver whilst thus moistened with muriatic acid, the silver blackens a little after a while at the spot on which the moistened mass rested.

* When hyposulphites are heated by means of the spirit-lamp, in a glass tube closed at one end, they are, like the sulphites, converted into a metallic sulphuret and a sulphate. At the same time, a little sulphuretted hydrogen is disengaged, besides the water of crystallisation of the salt, and a small quantity of sulphur is deposited.

* Hyposulphites, when thrown upon nitrate of potash in a state of fusion, disengage ruddy vapours of nitrous acid. But as most of them contain a great deal of water of crystallisation, they froth up very much.

* Before the BLOW-PIPE, the hyposulphites behave like the sulphate, both with a bead of soda and silica, and with a piece of silver, upon which they are thrown after having been exposed upon charcoal with soda to the action of the interior flame.

* Hyposulphites are so well characterised by their behaviour with muriatic acid and several other acids, that it is difficult to confound them with other salts. They differ from the hyposulphates and sulphites, because, when they are decomposed by means of an acid, they disengage sulphurous acid as the sulphites do; but they at the same time deposit sulphur, which the sulphites do not.

2. ACIDS OF SELENIUM.

1°. SELENIC ACID, SeO_3.

(Acide Sélénique.)

* AQUEOUS SELENIC ACID is a colourless liquid, of an oily consistence, which may be heated to 280° cent. (536° Fahr.) without undergoing decomposition. Exposed to a higher heat, it is converted into oxygen and selenious acid. When concentrated and mixed with water, it becomes hot, precisely as sulphuric acid in similar circumstances.

* The aqueous solution of selenic acid is not decomposed by sulphuretted hydrogen; but when aqueous selenic acid is boiled with muriatic acid it is decomposed, selenious acid is formed, and chlorine gas is disengaged, which may be recognized as such by its smell, and because it bleaches a strip of moistened litmus paper held above the liquor. This is the reason why a mixture of selenic and of muriatic acid, or of muriatic acid with a seleniate, dissolves platinum like aqua regia, owing to which platinum vessels must not be used with such a mixture.

* Aqueous selenic acid, like most aqueous acids, dissolves zinc and iron with disengagement of hydrogen; it has also the property of dissolving gold, but platinum is insoluble therein[1].

* With the bases selenic acid forms salts which have the greatest analogy to the corresponding sulphates: the acid and the neutral seleniates are soluble in water, excepting the combinations which selenic acid forms with baryta, strontia, lime, and protoxyde of lead, which are either insoluble or very sparingly soluble in that vehicle, and which, like the corresponding sulphates, do not dissolve in a free acid, in the cold. Wherefore the solution of A SALT OF BARIUM can as well be used for detecting selenic acid in an aqueous solution, or in that of one of its salts, as for detecting sulphuric acid. It is only necessary, in order to be convinced of the insolubility in free acids of the precipitate of seleniate of baryta obtained, to add nitric acid, and not

muriatic acid, because the latter has a decomposing action upon selenic acid [especially by boiling].

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[1] With the help of heat it also dissolves copper, and is thereby partially converted into selenious acid.—ED.

* When solutions of the seleniates are boiled for a long time with MURIATIC ACID, chlorine gas is disengaged, exactly as selenic acid does under similar treatment, and the selenic acid of the salt becomes converted into selenious acid[1].

* Solutions of the seleniates, and the aqueous solution of selenic acid, are not precipitated by either an aqueous solution or a current of SULPHURETTED HYDROGEN, unless they contain a metallic oxyde susceptible of being precipitated by it in the state of metallic sulphuret. When, however, before treating the solution of the salt by sulphuretted hydrogen, it has been boiled for a long time with muriatic acid, sulphuretted hydrogen produces the same decomposition as with selenious acid.

* An aqueous solution of SULPHUROUS ACID does not decompose solutions of the seleniates, nor that of selenic acid. The decomposition is, however, effected when they have been previously boiled for a long time with muriatic acid; selenic acid is then converted into selenious acid, and is decomposed in the same manner as this latter acid would be by such treatment[2].

* The presence of selenic acid in the seleniates, which are insoluble in water and in acids, may be determined in the same manner as that of sulphuric acid in the corresponding sulphates; but it is easier to boil the insoluble seleniate with muriatic acid for the purpose of converting the selenic into selenious acid, the presence of which may subsequently be recognized: a long time is, however, required completely to effect this conversion.

* Almost all the seleniates being soluble in acids, the reduction is complete when the compound has been dissolved in muriatic acid. But if the selenic acid should be combined with protoxyde

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[1] In this reaction part of the oxygen of the selenic acid combines with the hydrogen of the muriatic acid to form water, and the chlorine of the muriatic acid is set free, the selenic acid being at the same time converted into selenious acid.—ED.

[2] That is to say, in order to precipitate the selenium from selenic acid, it must be boiled with muriatic acid until chlorine gas has ceased to be evolved, by which it is converted into selenious acid, and then, upon adding aqueous solution of sulphurous acid, selenium is precipitated.—ED.

of lead, the solution cannot be complete, because some protochloride of lead is formed.

* When a soluble seleniate, or even an insoluble one,—for example, seleniate of baryta,—is introduced into a sulphuric acid solution of indigo, sufficiently dilute to have only a slight bluish colour, and sulphuric acid is further added, the solution is decolorised by boiling the whole. This bleaching takes place also when, instead of sulphuric acid, muriatic acid is employed, because chlorine is set free, which decolorises the solution of indigo.

* When seleniates, in the solid form, are mixed with muriate of ammonia, and the whole is heated in a small retort, selenium is sublimed [and condenses in the cool part of the neck of the retort[1]].

* Before the BLOW-PIPE the seleniates behave like the sulphates either with a bead of soda and silica, or with a piece of silver upon which they are thrown after treatment with soda upon charcoal in the interior flame. When these salts are fused upon charcoal with soda in the interior flame, they exhale an odour of decayed horse-radish, which is characteristic. They emit likewise this odour very powerfully when heated with microcosmic salt.

* SELENIC ACID, either free or in solutions of seleniates, can be confounded with no other substance except sulphuric acid, in consequence of its behaviour with the solution of a salt of barium; but it is distinguished by its deportment with muriatic acid, which is not decomposed by sulphuric acid.

2°. SELENIOUS ACID, SeO_2.

(Acide Sélénieux.)

* SELENIOUS ACID is obtained by dissolving selenium in aqua regia or in nitric acid. In the pure aqueous state it forms

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[1] In this way can also a mixture of sulphuric and of selenic acid be separated. To effect this, the solution of sulphuric and of selenic acid must be saturated with potash, and the dried residuum mixed with sal ammonia; heated in a retort, as just said, the selenic acid is decomposed by the ammonia, and selenium is reduced.—ED.

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crystals which resemble nitrate of potash, and at a temperature a few degrees below the boiling point of sulphuric acid, it is sublimed without decomposition under the form of an anhydrous crystalline mass. In the gaseous state, this acid has a feeble yellowish-green colour[1]. It is very soluble in water; its concentrated solution in hot water crystallises on cooling. It is also soluble in alcohol[2].

* The selenites, whose base is an alkali, are all soluble in water. The solutions of the neutral alkaline selenites have an acid reaction. Some of the neutral compounds of selenious acid with the earths and the metallic oxydes are insoluble; others are very sparingly soluble in water. They are soluble, however, in free acids; but several of them are likewise insoluble in acids, or almost so; such is the case, for example, with the selenites of lead and those of silver, which are insoluble in nitric acid. All the acid selenites appear to be very soluble in water.

* The neutral soluble selenites are precipitated by the solutions of BARYTIC SALTS; but the precipitate, which is selenite of barium, re-dissolves in free acids.

* The solutions of selenites in water or in acids, and that of selenious acid, do not undergo any change by boiling with MURIATIC ACID.

* A solution or a current of SULPHURETTED HYDROGEN produces in a dilute solution of selenious acid, and likewise in solutions of selenites rendered acid by muriatic or by any other acid, provided these solutions do not contain any metallic oxyde precipitable from such acid solutions by sulphuretted hydrogen, a lemon-yellow precipitate of sulphuret of selenium which becomes deep yellow, almost cinnabar-red, by heating the liquor, and which assumes that colour also by drying.

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[1] Berzelius says, that gaseous selenious acid has a deep yellow colour, which perfectly resembles that of chlorine.—ED.

[2] Selenious acid is largely soluble in alcohol, and when such a solution is distilled, a small quantity of selenium is reduced, and the product has an ethereal odour. According to Berzelius, if the alcoholic solution of selenious acid be mixed with sulphuric acid, and the mixture subjected to distillation, an alcohol mixed with a volatile substance passes over, which has an insupportable smell, whilst a considerable quantity of selenium is reduced.—ED.

If HYDROSULPHURET OF AMMONIA be poured in the solution of a neutral or of an alkaline selenite, a yellow precipitate of sulphuret of selenium is likewise formed, but which is very soluble in an excess of the re-agent.

* When an aqueous solution of SULPHUROUS ACID is poured in an aqueous solution of selenious acid, or in either an aqueous or an acid solution of a selenite, the selenious acid is reduced; after a time, selenium separates under the form of a cinnabar-red powder, which, by remaining for a long time in suspension, renders the liquor turbid, and of a red colour; after a longer time, red flakes are deposited. If the liquor be submitted to a prolonged ebullition, the particles of reduced selenium gather together, become black, and contract into a very small bulk. The reduction of selenious acid is effected in the same manner, and better still, when the solution of a sulphite is gradually poured in its solution, or in that of a selenite; yet if the solution of the selenite is neutral, it is necessary to add some acid to it, previously to treating it as just said, because the solution should be acid. It is often a difficult and long operation to effect the reduction of very small quantities of dissolved selenious acid into metallic selenium by means of sulphurous acid. This is especially the case when the liquor contains much nitric acid. It is then necessary to add muriatic acid by degrees to such a liquor, to boil it, and then to add again the solution of a sulphite, and again to boil the whole; the selenium may thus be precipitated, but it often occurs that a long time is required to effect this[1].

* A bar of METALLIC ZINC plunged in solution of selenious acid, or in solutions of selenites, rendered slightly acid by the addition of an acid, precipitates selenium; but the precipitation is not complete. The zinc becomes at first covered with a film of a copper colour, and afterwards the precipitated selenium separates under the form of red, brown, and blackish flakes[2].

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[1] Berzelius recommends, after the addition of muriatic acid, to evaporate the liquor with precaution, in order to decompose and volatilise the nitric acid, to re-dissolve the dry salt, and then to precipitate it by sulphurous acid.—ED.

[2] These variations in the colour of the precipitate are dependent upon the temperature at which the precipitate has been formed.—ED.

* The presence of selenious acid in the selenites, which are insoluble in water, but which have been dissolved by means of muriatic acid, is detected by the behaviour of such a solution towards sulphuretted hydrogen and sulphurous acid. When selenites contain metallic oxydes, which are likewise precipitable by these two re-agents, they should be separated from the selenious acid by treatment with hydrosulphuret of ammonia, or in some other way; muriatic acid being subsequently added to the solution in hydrosulphuret of ammonia, precipitates sulphuret of selenium. When the selenites which are insoluble in water are insoluble also in muriatic acid, nitric acid must be employed to dissolve them.

* When selenites in the solid form are mixed with muriate of ammonia, and the whole is heated in a small retort, a sublimate of selenium is obtained.

* If selenites which contain even traces only of organic matter are exposed to a low red heat, a certain quantity of the salt is reduced into selenium; and if the selenites are soluble they may be dissolved subsequently, and the solution has a slightly reddish colour. If a selenite of fixed alkali or of an earth be mixed with pulverised charcoal, and exposed to a red heat, there is a reduction of selenium.

* Before the BLOW-PIPE, the selenites behave like the seleniates (page 221), and like them are easily recognized.

* The red precipitate which sulphurous acid produces in selenious acid, and in the solutions of the selenites rendered acid, enable the analyst easily to recognize these salts, and does not allow of their being confounded with other substances. Selenium itself does not behave in a less characteristic manner, but, for greater safety, the reduced selenium may be submitted to fresh examination[1].

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[1] Selenious acid is less volatile than either muriatic or nitric acid, and displaces them from their combinations with powerful bases; but selenious acid is displaced from its combinations with the said bases by sulphuric, phosphoric, arsenic, and boracic acids.—ED.

3. ACIDS OF TELLURIUM.

1°. TELLURIC ACID, TeO_3.

(*Acide Tellurique.*)

* Telluric acid may, according to Berzelius, be obtained in large crystals[1]. It is very soluble in water, though slowly. Its dilute solution reddens litmus paper, but with difficulty. This solution has a metallic non-acid taste. Telluric acid is soluble in aqueous alcohol, but not in anhydrous alcohol, and its saturated aqueous solution is precipitated by alcohol. The crystallised acid loses part of its water at a temperature somewhat higher than 212° Fahr., and it then dissolves very slowly but completely in water, especially if boiling. When heated more strongly, but not to redness, it loses all its water, assumes an orange-yellow colour, and becomes completely soluble in cold water, in boiling water, and in boiling nitric acid. When it is treated in this state by a boiling hot solution of pure potash, it combines with that alkali, but does not dissolve unless the liquor is very concentrated. Exposed to a still higher temperature oxygen is disengaged, and it becomes converted into tellurious acid.

* Amongst the salts which telluric acid forms with the bases, the tellurates of alkalies are soluble in water, and also slightly so in alkaline solutions. Water being added to the aqueous solution does not produce any precipitate. When these salts are exposed to a temperature below redness, they often become absolutely insoluble in water. Most earthy and metallic tellurates are insoluble.

* When tellurates are exposed to a red heat, they fuse, and are converted into tellurites under disengagement of oxygen gas.

* Tellurates can be dissolved in cold muriatic acid without

undergoing decomposition. Water may be added to this solution without rendering it milky, even though there should be a slight excess of muriatic acid. If, however, it be boiled, chlorine is disengaged, and an addition of water may then determine a white precipitate of tellurious acid, provided there be not too great an excess of acid, which would hinder the precipitation.

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[1] These crystals are hexagonal prisms, with two faces larger than the others, and very obtuse four-sided summits. The crystals, however, are often cruciform, and striated like saltpetre. The crystallised acid is a combination of 1 atom of acid with 3 atoms of water, $TeO_3 + 3$ aq. The effloresced acid contains 1 atom of acid + 1 atom of water, $TeO_3 +$aq.—Ed.

* When muriatic acid is poured in aqueous solutions of tellurates, and a solution of *sulphurous acid* or of an *alkaline sulphite* added, and the mixture then heated, metallic tellurium is separated under the form of a black precipitate. The same thing happens with a muriatic acid solution of tellurates which are insoluble in water.

* If a solution of CHLORIDE OF BARIUM be poured in solutions of neutral tellurates, a bulky white precipitate of tellurate of baryta is produced, which after a time becomes granular and heavy, and which is insoluble in muriatic or nitric acids.

* When a current of SULPHURETTED HYDROGEN is passed through a very dilute solution of telluric acid, no change is at first produced; but if the liquor be left standing in a well-stopped bottle, in a warm place, after a time it becomes of a light-brown colour, and ultimately the side of the bottle becomes covered with a coating of sulphuret of tellurium having a metallic lustre; the liquor is then limpid and colourless.

* When tellurates are exposed to a red heat with charcoal and an alkali, fixed metallic tellurates are formed, which yield a solution having the colour of red wine.

* Before the BLOW-PIPE telluric acid is recognised in tellurates, in the same manner as tellurious acid in tellurites, into which they are converted by the action of a red heat.

* Telluric acid may be detected in its salts by its behaviour towards muriatic acid and sulphurous acids. The solubility of tellurate of baryta in acids is sufficient to distinguish it from the sulphate and seleniate of baryta.

2°. TELLURIOUS ACID, TeO_2.

(Oxyde Tellurique);

or,

(Acide Tellureux.)

* In the pure state tellurious acid has a white colour, it fuses at an incipient red heat, and then forms a limpid liquid of a deep yellow colour. The mass retains its yellow colour whilst hot, but after cooling it is white and strongly crystalline. When tellurious acid is heated to redness in contact with the air, it is completely volatilised. The sublimate is not crystalline, at least in the small way, and a much stronger heat is necessary to volatilise it than that required for sesquioxyde of antimony, with which it has some resemblance. It is easily reduced into metallic tellurium by charcoal[1].

* Tellurious acid is slightly soluble in nitric acid, but a notable quantity of it cannot be dissolved unless it be put in contact with metallic tellurium in powder. When such a solution is diluted by water, a white precipitate of aqueous tellurious acid is produced. When, however, the solution is heated before adding the water, or if it be left at rest for several hours, the dissolved tellurious acid is deposited in the anhydrous state, under the form of crystalline grains, and the acid retains only a very small quantity of it, which cannot be precipitated by pouring water in the liquor.

* Anhydrous tellurious acid is very sparingly soluble in water, and the solution does not redden litmus paper. It is likewise but sparingly soluble in acids in ammonia, and in the solutions of alkaline carbonates, unless it be boiled for a long time in these liquids. On the contrary, it is soluble in solutions of pure potash or soda.

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[1] That is to say, by fusing it upon charcoal the reduction is effected with a slight detonation, and the greatest part of the tellurium is volatilised. If mixed with charcoal in a closed crucible, it is easily reduced, but the metal is in a state of extreme division.—Ed.

* Aqueous tellurious acid is very soluble in muriatic acid. It dissolves slowly in ammonia; is very soluble in solution of hydrate of potash, and dissolves by boiling in solution of fixed alkaline carbonates.

* Hydrated tellurious acid is obtained by treating a recently-prepared nitric acid solution of tellurium or the chloride of tellurium by water, or by fusing anhydrous tellurious acid with an equal weight of carbonate of potash, keeping the mass in fusion until all disengagement of carbonic acid has ceased, dissolving in water the tellurite of potash thus produced, and adding nitric acid to the liquor until it begins sensibly to redden litmus paper. It is white, light, earthy, and not crystalline; it reddens moist litmus paper, and in the humid state it dissolves in notable quantities in water. This solution likewise reddens litmus paper; but when heated, anhydrous tellurious acid is separated in a granular state, and then the liquid no longer reddens litmus paper. Hydrated tellurious acid likewise loses its water when slightly dried, and becomes anhydrous tellurious acid.

* Hydrated tellurious acid dissolves easily in nitric, muriatic, and other acids. The nitric acid solution is the only one from which anhydrous tellurious acid is separated by time or heat. This phenomenon is not produced with the solution in other acids.

* If water be added to the solutions of tellurious acid in acids, especially to that in muriatic acid, a precipitate of aqueous tellurious acid is formed, provided these solutions do not contain too much free acid, precisely as is the case with the solutions of sesquioxyde of antimony in muriatic acid. This precipitate re-dissolves in a free acid.

* If to a solution of hydrated tellurious acid in muriatic acid, a solution of POTASH, AMMONIA, CARBONATE OF POTASH, BICARBONATE OF POTASH, OR CARBONATE OF AMMONIA be added, an abundant white precipitate of aqueous tellurious acid is obtained, completely soluble in an excess of the re-agent. The solution of tellurious acid treated by an excess of carbonate of potash,

sometimes becomes greenish by long standing. This colour vanishes by heating, but re-appears upon cooling.

* A solution of PHOSPHATE OF SODA produces a white precipitate, even in acid solutions of tellurious acid[1].

* A solution of OXALIC ACID produces no precipitate.

* A solution of FERROCYANURET OF POTASSIUM, nothing.

* A solution of FERRICYANURET OF POTASSIUM, nothing.

* HYDROSULPHURET OF AMMONIA poured in a solution of tellurious acid saturated by an alkali, gives a brown precipitate of sulphuret of tellurium, which, in large quantities, appears almost black. This precipitate redissolves with great facility in an excess of the re-agent.

* The aqueous solution, or a current of sulphuretted hydrogen, determines in an acid solution of tellurious acid, an immediate brown precipitate of sulphuret of tellurium, which, in point of colour, resembles much that which sulphuretted hydrogen gas produces in solutions of protoxyde of tin.

* A solution of SULPHUROUS ACID, or of a SULPHITE OF ALKALI, determines in the acid solutions of tellurious acid a black precipitate of metallic tellurium. When the quantity of tellurious acid is inconsiderable, this precipitate appears only after a certain time, or by heating the liquor.

* A bar of METALLIC ZINC plunged in solutions of tellurious acid, precipitates tellurium in the metallic state, under the form of a voluminous black mass.

* The solutions of the soluble compounds of tellurious acid are precipitated by INFUSION OF GALLS; this character distinguishes them from solutions of tellurates, which are not precipitated by this re-agent.

* Most of the compounds of tellurious acid which are insoluble in water, are soluble in muriatic acid. These solutions are ordinarily yellow, and do not emit the odour of chlorine when heated, which circumstance distinguishes them from the combinations of telluric acid. When there is not too much muriatic

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[1] That is to say, if the acid in which the solution of tellurious acid is effected be in slight excess.—ED.

acid, the solution precipitates hydrated tellurious acid as soon as water is added. Tellurious acid may also be precipitated from these solutions by sulphuretted hydrogen, or by sulphurous acid, and the substance which was combined with the tellurious acid may be found in the filtrate, provided always that this substance is not precipitable by sulphuretted hydrogen, or by sulphurous acid. The combinations of tellurious acid with the alkalies are all soluble in water; the combinations with other bases are either insoluble or sparingly soluble.

* Tellurious acid may be easily detected in its combinations, by exposing them to a red heat in conjunction with alkali and charcoal, an operation which, for small quantities, must be performed in glass tubes closed at one end. The mass thus obtained is then to be treated by water, by which means a red solution of telluride of potassium or of sodium is obtained.

* Before the BLOW-PIPE tellurious acid is recognised by the extreme facility with which it is reduced upon charcoal in the interior flame; the reduced metal is very easily volatilised and reoxydated, and covers the charcoal with a white fur. In order to distinguish by means of the blow-pipe tellurious acid from sesquioxyde of antimony, it must be heated in a glass tube open at both ends. The tellurious acid sublimes on the upper and coldest part of the tube under the form of a white smoke, which, where it is heated, fuses into small drops; which phenomenon, however, can be well observed only when the layer formed by the sublimate is not too thin. Oxyde of antimony sublimed in the same manner in a glass tube opened at both extremities, forms likewise a white smoke, but which can be removed from one place, and shifted to another by application of heat, so that the place occupied at first by the sublimate becomes empty. The two oxydes may likewise be distinguished from each other, because the white coating formed by oxyde of antimony upon charcoal disappears in the reducing flame, imparting at the same time a bluish tinge to the flame, or not colouring it at all, whilst tellurious acid communicates a fine green colour to the flame.

* The solutions of tellurious acid are easily recognised by their behaviour towards sulphuretted hydrogen, and likewise by the brown precipitate produced by hydrosulphuret of ammonia, which precipitate is very soluble in an excess of the re-agent. Solutions of protoxyde of tin are the only ones with which they might in this respect be confounded. It is true that hydrosulphuret of ammonia determines also a brown precipitate in solutions of protosalts of tin (page 173); but this precipitate is much less soluble in an excess of the re-agent; and besides, solutions of protosalts of tin differ from solutions of tellurious acid by their behaviour towards ammonia, the alkaline carbonates, and especially solution of gold (pages 170—174), in which tellurious acid forms no precipitate of purple of cassius. In general, tellurious acid differs by its volatility from almost all the other acids in the solutions of which hydrosulphuret of ammonia determines a precipitate susceptible of being dissolved by an excess of the re-agent. It is distinguished from oxyde of antimony (before the blow-pipe) by the characters which have been described above, and in its solutions by the colour of the precipitate produced by sulphuretted hydrogen. It is impossible to confound tellurious acid with the acids of arsenic.

4. ACIDS OF NITROGEN.

1°. NITRIC ACID, NO_5. ← N_2O_5 + Hω

(Acide Nitrique.)

Nitric acid has not been obtained yet in the anhydrous state. It forms with water a limpid liquid, and when in the highest state of concentration it volatilises at a temperature below that of boiling water; but when it contains more water, in which state it is most frequently met with, a temperature which may be as high as 120° cent. (248° Fahr.) is required to make it boil, and even 125° cent. (257° Fahr.) when glass vessels are used. * When, however, it contains more water, still its boiling point diminishes in proportion as the quantity of water is more considerable. Nitric acid in the highest state of concentration is very easily decomposed; when distilled it disengages ruddy vapours of nitrous acid, and assumes a yellow tinge. Exposure to solar light, and other influences, give it a yellow colour, the manifestation of which is accompanied by a disengagement of oxygen.

Nitric acid, diluted with water of the strength which ordinarily constitutes commercial nitric acid, oxydises most substances. Nearly all metals are oxydised by it; this acid being partially decomposed, and ordinarily converted into nitric oxyde, more rarely into nitrous oxyde, or nitrous acid. * The nitric oxyde escapes in the form of a gas, and by absorbing oxygen from the air, becomes nitrous acid. This is the reason why ruddy vapours are disengaged when a metal is treated by nitric acid. Even those metals which, by dissolving in other dilute acids, disengage hydrogen gas, produce these phenomena when oxydised by nitric acid; nearly all the metallic oxydes thus produced dissolve in the portion of acid which has not undergone decomposition; the only exceptions are peroxyde of tin, and oxyde of antimony, and also tellurious acid.

A few metals, namely: platinum, rhodium, iridium, and gold are not attacked by nitric acid; most metals are not oxydised by nitric acid in the highest state of concentration; such is the case more especially with copper and iron, but it oxydises zinc. Organic substances are likewise oxydised by nitric acid, most of which, when the reaction is promoted by the application of heat, and by the use of an aqueous acid, are converted into carbonic, malic, and lastly into oxalic acid; during these operations the nitric acid does not become coloured, if there be an excess of it.

* An excess of acid in the highest state of concentration converts organic substances into carbonic acid and water.

Many organic substances assume a characteristic yellow colour when treated by a less quantity of nitric acid than would be requisite completely to oxydise them; such is the case, for example, with the human skin, and with the corks of bottles which contain nitric acid.

Nitric acid forms very soluble salts, with nearly all the bases;

wherefore they cannot be precipitated from their solutions by pouring into them solutions of other salts. Only a few oxydes which have been enumerated just above (peroxyde of tin, oxyde of antimony, and tellurious acid) are not soluble in this acid. Nitric acid is, therefore, more difficult to detect than other acids, whether greatly diluted with water, or in the solutions of nitrates, when only a small portion of these salts can be obtained for examination.

The best method to detect very minute quantities of solutions of nitrates consists in evaporating the solution to dryness by means of a gentle heat, and to examine the dry residuum in the manner which will be mentioned below. When a solution contains free nitric acid, it is to be saturated with a base, in preference with potash, the solution is to be evaporated to dryness, and the dry residuum is to be submitted to the same treatment.

The methods employed for the detection of nitric acid, or of nitrates in solutions, are the following:

To the solution of the nitrate, add some muriatic acid, and a little GOLD-LEAF; by the help of heat the gold-leaf will then be dissolved, and will communicate a yellowish colour to the liquor. If the gold-leaf does not dissolve, it is a proof that no nitric acid is present[1].

* To ascertain whether any gold has been dissolved, the liquor is to be filtered, and the filtrate is to be tested by protochloride of tin (page 170).

To the liquid in which the presence of nitric acid, or of a nitrate, is suspected, add a quantity of concentrated sulphuric acid, which must not be much less than the fourth part of the liquid under examination. When the mixture has become cold, a small portion of PROTOSALT OF IRON is to be added, for which purpose a crystal of protosulphate of iron is to be preferred. * The nitric acid is converted by the first portions of the protosalt of iron into nitric oxyde, which, even if only a very small quantity of nitric acid be present, will impart a deep blackish-brown colour to the portion of solution of protosalt of iron, which may be subsequently added. The dark colour of the liquid disappears after some time. This method is, according to Richemont, the most delicate of all to detect the minutest traces of nitric acid; it is, however, necessary to add a large quantity of sulphuric acid, without which the experiment does not succeed[1].

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[1] Chlorates, perchlorates, chromates, bromates, &c., mixed with muriatic acid, have also the property of dissolving gold-leaf.—ED.

* Concentrated nitric acid imparts a yellow colour to quills, which effect is not produced by the dilute acid, according to Runge, even at a temperature of 100° cent. (212° Fahr.) If, for example, after having heated a piece of china by holding it in steam of water, a drop of very dilute nitric acid be placed therein, and a few scrapings from a quill pen be projected in this drop of dilute acid, they will turn very sensibly yellow after its evaporation. When there is only a very small portion of acid, the yellow colouring appears only at the extremities, or edges, of the scrapings; but if there be more acid, their whole surface is yellow. The solutions of neutral nitrates, even of those which redden litmus paper, have not this property, by means of which free nitric acid may be distinguished from its compounds. Muriatic acid does not possess this property either; and, therefore, this test may be employed to detect the smallest quantities of nitric acid which it might contain.

Small quantities of nitric acid or of nitrate may likewise be detected by mixing the liquor which contains them with a sufficient quantity of solution of indigo in sulphuric acid, to communicate a slight bluish tinge to it, adding a little sulphuric acid and boiling the whole. Thus treated the liquor becomes decolorised, or if there is but a small quantity of nitric acid present, it loses its blue colour and becomes yellow. By adding a little chloride of sodium (common salt) to the liquor before heating it, we may easily detect one five-hundredth part of nitric acid. This method has been indicated by Liebig, but it is inferior to the former[1].

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[1] It is also necessary to put a sufficient quantity of protosalt of iron, else on agitating the liquid the colour may disappear, on account of the whole of the protoxyde passing into the state of a peroxyde, which produces no colouring. If the mixture be very dilute, it is necessary to apply heat in order to produce the colouring in question; but the heat must not be continued too long, else the colour will also disappear.—Ed.

When the substance under examination is a solid nitrate, the presence of nitric acid therein may be recognised as follows:—

If the nitrate be mingled with CHARCOAL POWDER and the mixture heated in a small porcelain crucible, it fuses, and sparks of fire are emitted. This method is usually resorted to for the purpose of detecting the presence of nitric acid in the nitrates[2].

* The best manner of conducting the experiment consists (when the nitrate is very fusible, for example, nitrate of potash) in fusing it in a small porcelain crucible, and to project upon the fused mass small quantities of organic bodies containing carbon, for example, wood or paper, which become violently oxydised, producing at the same time a vivid deflagration. If the nitrate be more powerfully heated, and some pulverised sulphur be projected in the fused mass, the sulphur burns with a flame (not blue) but yellowish white, and so bright and dazzling that the eye can hardly bear it.

When nitrates are mixed with COPPER FILINGS, and if, the mixture being introduced in a tube of white glass closed at one end, a portion of concentrated sulphuric acid previously diluted with a small quantity of water, be poured upon it, ruddy fumes of nitrous acid are disengaged at the ordinary temperature. If concentrated sulphuric acid be poured upon the nitrates without using copper filings, colourless vapours of nitric acid are evolved which produce a white cloud when a glass rod moistened with ammonia is held at the surface[3].

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[1] It is inferior especially, because other substances, such as free chlorine, the chlorates and other substances, may also decolorise sulphate of indigo, and therefore this is no certain test of the presence of nitric acid.—ED.

[2] The chlorates deflagrate also when treated in this manner. Dr. Fresenius remarks, that if pulverised cyanide of potassium be mixed with a nitrate, and heated on a foil of platinum, a vivid deflagration will take place even though only very minute portions of nitrate be present.—ED.

[3] It should be remembered that sulphuric acid often contains traces of nitric acid, the absence of which latter acid should be ascertained before using this test. The absence of nitric acid may be readily ascertained by boiling the sulphuric acid with a small quantity of solution of indigo. If the blue colour remains unchanged, the absence of nitric acid may in most cases be inferred.—ED.

If a little zinc be dissolved in mercury so as only to diminish the liquidity of the mercury, and a small portion of this amalgam be placed in a small porcelain capsula, and if a solution of neutral protochloride of iron be then poured upon it in sufficient quantity to cover it, a small portion of nitrate projected through the liquid upon the mercury produces, after some time, a black mark on the spot where the salt rested. This method, which was indicated by Runge, may serve to detect very small quantities of a solid nitrate. Liquids containing nitric acid, or a nitrate, likewise impart a black colour to the amalgam in several places, but the reaction is less sensible than with the solid salts.

All nitrates are decomposed by exposure to a red heat[1]. Some of them when calcined disengage, first, oxygen gas, and are converted into nitrites, which again are decomposed by a stronger heat. Other nitrates, especially those the base of which is a metallic oxyde, disengage oxygen and nitrous acid when exposed to a red heat. If therefore the latter nitrates be introduced in a tube of white glass closed at one end, and heated therein by a spirit-lamp, the tube becomes filled with ruddy fumes indicating the presence of nitric acid. There are only a few of the nitrates which, when exposed to a red heat, part with their nitric acid in company with their water of crystallisation, without the acid being decomposed. Nitrate of ammonia is converted by heat into nitrous oxyde and water.

Of the experiments which have just been related, that by means of copper filings and sulphuric acid, and that by means of sulphuric acid and a protosalt of iron, give the most certain results for the purpose of detecting nitric acid in the nitrates; for the phenomena which the other re-agents produce may also take place with other substances[2].

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[1] The nitrates whose base is an alkali are decomposed by a red heat, with disengagement of oxygen mixed with nitrogen. The other nitrates disengage oxygen and ruddy fumes of nitrous acid or hyponitric acid.—Ed.

[2] M. Berthémot has proposed an easy method of detecting nitric acid, which consists in pouring in a glass 50 or 60 gr. measure of concentrated sulphuric acid free from nitric acid, and then a few drops of the liquor in which the presence of

* The recent researches of M. Millon modify, in an important manner, the characteristics which have been assigned to nitric acid.

* The process which is generally adopted for the preparation and purification of nitric acid does not eliminate a certain quantity of nitrous acid which, according to M. Millon, exercises a very great influence upon its properties. Traces of nitrous acid in the most dilute nitric acid are sufficient to cause the precipitation of iodine from iodides, of sulphur from monosulphurets, and from the aqueous solution of sulphuretted hydrogen; to change the colour of protosalts of iron into brown, and to destroy the colour of sulphate of indigo, whilst the pure nitric acid, which is free from nitrous acid, produces none of these effects.

* When nitric acid contains no organic matter, it may be freed from nitrous acid by putting aside the first products of the distillation, which contain all the nitrous acid; but the best method, even when the acid contains organic substances, consists in distilling it with a certain quantity of bichromate of potash; the proportion being one part of bichromate for 100 of nitric acid, which proportion suffices in most cases when the density of the acid is not above 1·48; by this process the nitrous acid is oxydised at the expense of the oxygen of the chromic acid, and is converted altogether into nitric acid.

* In order to prepare a more concentrated nitric acid, M. Millon prescribes to distil the commercial acid, so as to separate the first third part which contains the most aqueous portion,

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nitric acid is suspected. The whole is to be stirred with a glass rod, and with the moist extremity of the rod a small particle of *brucine* is taken up and transferred to the acid in the glass; the whole is to be well stirred. If any nitric acid be present, the liquid becomes red and afterwards yellow. If no nitric acid be present, the brucine does not dissolve. The presence of $\frac{1}{10000}$ of nitric acid may thus be detected.—Mr. O'Shaughnessy has also proposed a very delicate test, founded on the orange-red colour, which afterwards becomes yellow, which nitric acid imparts to morphia. The supposed nitrate is to be heated in a test-tube with a drop of sulphuric acid, and then a crystal of morphia is added. Of course, the absence of nitric acid in the sulphuric acid employed must be ascertained, which may be done by testing the sulphuric acid with morphia in another tube.—Ed.

and then to complete the distillation, after having added to the residuum its own bulk of concentrated sulphuric acid. The nitric acid thus obtained must now be deprived by a second distillation of the sulphuric acid, which has passed over in the first distillation, and it has then the highest possible density; but it contains much nitrous acid in solution, which may be eliminated by passing through it a current of dry carbonic acid, the temperature being kept near the boiling point.

* Thus purified, it is colourless, and very fuming; diluted with two or three times its bulk of water, it produces no cloudiness in the aqueous solution of sulphuretted hydrogen; its density is 1·552 at +20° cent. (68° Fahr.); its composition is exactly represented by NO_5HO.

* According to M. Millon, dilute nitric acid, of a density 1·070 for example, when perfectly pure, has no action upon copper at a temperature of +20° (68° Fahr.); but if a current of nitric oxyde be passed through this liquid, or if a few drops of a solution of nitrite of potash is poured in it, the copper is immediately attacked, and the whole of the metal is ultimately dissolved, provided the quantity of acid be sufficient.

* Temperature, however, has a great influence upon the oxydisement of metals by nitric acid: at 16° or 20° cent. below zero (from above 4° above, to 4° below 0 Fahr.), copper, for example, is not attacked by any of the hydrates of that acid.

* Bismuth and tin retain their metallic lustre at a temperature of +20° cent. (68° Fahr.) in the acid which contains one or two equivalents of water: the same is the case with iron. These metals are attacked with violence by a less concentrated nitric acid, but iron remains untouched in presence of a pure acid, which contains as much as 4½ equivalents of water.

* Zinc is always attacked at a temperature of +20° cent. (68° Fahr.) by pure nitric acid, whatever may be its degree of concentration or of dilution.—E. Peligot.

2°. NITROUS ACID, NO_3.

(Acide Nitreux.)

Pure nitrous acid is liquid when it has been condensed by the application of an intense cold, in which state it is of a deep green colour, but if exposed to a still more intense cold, it is colourless. It is very volatile. At the ordinary temperature it is gaseous, and has a deep reddish-yellow colour. It is never met with in the pure state in chemical analysis, but combined with nitric acid it is of frequent occurrence, and the mixture constitutes the acid which some chemists consider as a particular degree of oxydisation, and which they call nitrous acid, whilst they give the name of hyponitrous to the true nitrous acid.

Nitrous acid dissolves in water, but it then undergoes partial decomposition: nitric oxyde is disengaged, and a combination composed of nitric and of nitrous acid and of water is formed.

The compounds of nitrous acid with bases cannot be obtained in a direct manner. They much resemble the nitrates, and like them, they deflagrate when heated in conjunction with pulverised charcoal. They may, however, be distinguished from the nitrates by the following methods:—

If to the solutions of a nitrate, muriatic acid and gold-leaf be added, the metal does not dissolve, unless they at the same time contain a nitrate. It is true that the liquid has a slightly yellowish tinge when concentrated; but this colour is not owing to any gold dissolved, and it vanishes upon addition of water.

* If sulphuric acid or acetic acid be added to solutions of the nitrites, nitrous acid is set at liberty; but it is immediately converted into nitric acid, which remains in solution, and in nitric oxyde, which escapes in the gaseous state, producing ruddy fumes of nitrous acid on coming in contact with the air. The nitrites are not decomposed by carbonic acid.

When solutions of the nitrites are subjected to distillation, provided the boiling is carried on slowly, nitric oxyde is disengaged, which on coming in contact with the air is converted into ruddy vapours of nitrous acid, and the nitrite in solution is converted into a nitrate. When solutions of the nitrites are boiled in contact with the air, they are easily converted into nitrates.

* When a solution contains nitrous acid, or when a nitrite is treated by sulphuric acid and a PROTOSALT OF IRON, as is done for the purpose of detecting nitric acid or a nitrate (page 233), the same phenomena are produced, but the first drops of the solution of protosulphate of iron immediately produce the deep blackish-brown colour, while in the case of nitric acid this characteristic colour is produced only at the moment of the second addition of the iron solution.

* The solutions of the nitrites, the base of which is an alkali or an alkaline earth, restore the blue colour of reddened litmus paper.

Nitric acid is about the only acid with which the compounds of nitrous acid may be confounded; but the characteristics which have been mentioned are sufficient to distinguish the one from the other.

The *combination of nitrous with nitric acid* which, as above said, some chemists consider as a particular acid, is contained in fuming nitric acid. This latter acid, according to Mitscherlich, is a solution of nitrous acid in nitric acid. It is almost entirely decomposed by water; the nitrous acid which it contains is transformed into nitric acid, and nitric oxyde is disengaged. A small portion of nitrous acid always remains, however, in the fuming nitric acid, which has been diluted with water. The addition of a large quantity of water in fuming nitric acid destroys its peculiar reddish-yellow colour and it becomes colourless.

* If, however, only a small quantity of water be at first added, gradually increasing its proportion, the acid turns green, then blue, and lastly, it becomes colourless.

To the French edition the following remarks are added by E. Peligot:—

* Since the publication of this work, nitrous acid, NO_3 and

hyponitric acid, NO_4, have been the subject of fresh investigations, which whilst they have developed the true characters of these substances, most materially modify the notions which have just been given.

* Nitrous acid, NO_3, has never been obtained as yet in the pure state; it is never produced by the direct combination of nitric oxyde with oxygen, which was admitted to be the case a few years ago; the characters assigned by M. H. Rose to that acid are those of a mixture of nitrous and hyponitric acids.

* Hyponitric acid, NO_4, is obtained by heating dry nitrate of lead, or by the combinations of nitric oxyde gas with oxygen; collected in a vessel surrounded by a frigorific mixture it crystallises in colourless and transparent prisms, which begin to fuse at a temperature of —9° cent. (15·8° Fahr.); at the ordinary temperature it forms an orange-coloured liquid, which boils at 22° cent. (71·6° Fahr.); it is this acid which constitutes the *nitrous acid fumes*.

* By contact with water hyponitric acid presents several distinct phases of decomposition. If water be added by small portions at a time, the acid becomes green; and this colour is so much deeper as the proportion of water to the action of which it is submitted is larger; this proportion may actually be larger than the weight of the hyponitric acid, without any disengagement of gas being produced, for this acid is then decomposed into a hydrate of nitric acid, and in free nitrous acid, which remains in solution. By distilling this mixture at a very gentle heat, and condensing the more volatile product in a refrigeratory mixture, the indigo-blue liquid thus obtained boils at a temperature below 0° cent. (32° Fahr.), and consists mostly of nitrous acid; yet a certain quantity of hyponitric acid always passes over along with it; which latter acid can be eliminated only by rectifying large quantities of this blue liquid.

* If a still larger quantity of water is added to hyponitric acid a disengagement of nitric oxyde gas is produced, resulting from the decomposition of the nitrous acid at first formed; at

the same time, the liquor is decolorised, and it then contains nothing but dilute nitric acid.

* M. H. Rose indicates, as a means of detecting the nitrites, the use of acetic acid, which transforms them into nitrates under disengagement of nitric oxyde gas; this process is uncertain; at the ordinary temperature the nitrites are soluble without decomposition in acetic acid; it is only by heating the liquid, or when the chemical reaction developes heat, that a disengagement of nitric oxyde is manifested; I have taken advantage of this property to analyse the basic nitrite of lead by means of the peroxyde of that metal, the nitrite being first dissolved in acetic acid[1].

* The nitrite of silver being sparingly soluble in water, its production may serve to detect the soluble nitrites; this salt is precipitated in the form of silky crystals of a yellowish-white colour when concentrated solutions of nitrate of silver and of an alkaline nitrite are put in contact.

5. ACIDS OF CHLORINE.

1°. PERCHLORIC ACID, ClO_7.

(Acide Oxychlorique.)

* This acid is obtained by decomposing perchlorate of potash by means of hydrofluosilicic acid. When deprived of water as much as possible, it is, according to Sérullas, solid and crystalline at the ordinary temperature; it fuses at 45° cent. (113° Fahr.) By exposure it rapidly absorbs the moisture of the air, and emits thick white fumes. Its aqueous solution, when carefully evaporated, may be brought to a density of 1·65. It boils at 200° cent. (392° Fahr.) It is a limpid, colourless liquid, which reddens litmus paper, but without bleaching it, and it dissolves iron and zinc with disengagement of hydrogen gas.

* When liquid perchloric acid is mixed with concentrated SULPHURIC ACID it is almost wholly decomposed. The mixture becomes yellow, and if heated to ebullition, chlorine and oxygen

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[1] See *Annales de Physique et de Chimie*, 3rd series, vol. 2, page 87.

gases are evolved; whilst, at the same time, a small quantity of perchloric acid sublimes in the solid form.

* A solution of SULPHUROUS ACID, of SULPHURETTED HYDROGEN, or of MURIATIC ACID, does not decompose perchloric acid, even by boiling. Neither does ALCOHOL produce any change. A piece of paper saturated with the acid, even concentrated, does not ignite, but it acquires the property of scintillating and decrepitating, sometimes with detonation, when placed upon red-hot charcoal[1]. When perchloric acid is heated in a tube or in a retort until it boils, if a dry piece of paper be brought to the orifice of the tube so as to make it receive the vapours, the paper vividly and spontaneously inflames.

* The salts which perchloric acid forms with bases are very soluble in water; with the exception of perchlorate of potash and perchlorate of ammonia, most of them deliquesce in the air, and are likewise insoluble in alcohol. Perchlorates of potash, of ammonia, of protoxyde of lead, and of suboxyde of mercury are the only salts of this acid which are not deliquescent. Perchlorate of potash is very sparingly soluble in water, and absolutely insoluble in alcohol. It is a little less soluble than bitartrate of potash, owing to which, according to Sérullas, when perchloric acid is poured in a saturated solution of the latter salt a very slight precipitate of perchlorate of potash is produced.

* All the perchlorates are neutral. The solution of those the base of which is an alkali or an alkaline earth does not alter the colour of litmus paper.

* The perchlorates are not altered, at least at the ordinary temperature, by SULPHURIC ACID nor by MURIATIC ACID. When thrown upon ignited charcoal they scintillate more or less vividly. Those perchlorates the base of which is an alkali or an alkaline earth disengage oxygen when exposed to a red heat, and are converted into a metallic chloride; wherefore, solution of nitrate of silver produces a precipitate of chloride of silver in

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[1] The perchlorates being less fusible than the nitrates, generally burn less easily than the latter salts when thrown upon ignited charcoal.—ED.

the solution of a perchlorate which has previously been exposed to a red heat, whilst this re-agent does not trouble the solution of a pure perchlorate which has not been made red hot.

* The compounds of perchloric acid are easily recognised by the property which most of them possess of disengaging oxygen, and becoming converted into metallic chlorides by exposure to a red heat. We shall indicate further what are the means of distinguishing perchloric acid and its salts, from chloric acid and the chlorates.

2°. CHLORIC ACID, ClO_5.

(*Acide Chlorique.*)

Aqueous chloric acid is a colourless, or slightly yellowish liquid, which by a very gentle heat may be evaporated to the consistence of oil, which is better effected still, at the ordinary temperature, by placing it under a bell by the side of another vessel containing concentrated sulphuric acid[1]. Diluted with water, it first reddens litmus paper, and then bleaches it.

* When concentrated, a piece of paper plunged in it spontaneously ignites upon being taken out, and an odour somewhat resembling that of nitric acid is emitted, which odour, however, appears to be peculiar to concentrated chloric acid when heated. Chloric acid, like most other acids, dissolves iron and zinc with disengagement of hydrogen gas.

Chloric acid converts SULPHUROUS ACID into sulphuric acid, and is thereby resolved into chlorine.

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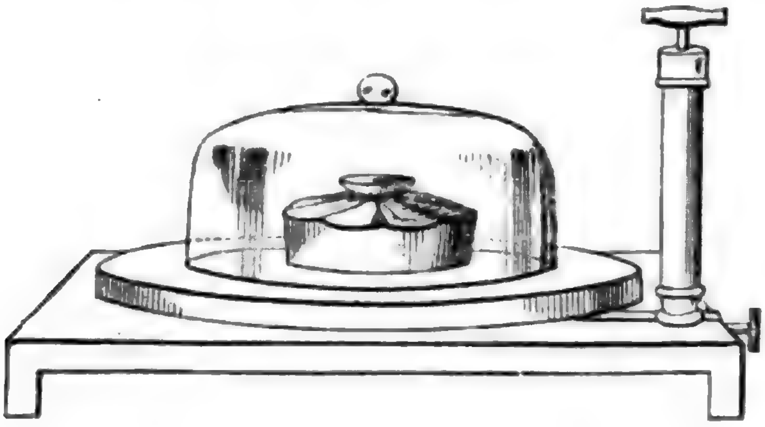
[1] This is still better performed by placing the aqueous chloric acid over a dish of concentrated sulphuric acid within the receiver of an air-pump, as in the figure. — Ed.



It converts SULPHURETTED HYDROGEN into sulphur and water.

It transforms MURIATIC ACID into chlorine and water.

These reactions essentially distinguish it from perchloric acid.

* Dilute chloric acid is very easily altered by alcohol and by ether, even at the ordinary temperature. The heat thus produced is considerable enough to make the liquids boil. When there is little alcohol and much acid, the action is so violent, that the alcohol bursts into flame; chlorine is disengaged, and acetic acid produced.

* When concentrated chloric acid is heated in a retort, it is decomposed; perchloric acid is formed, which distils over, and chlorine and oxygen gases are disengaged.

Chloric acid forms, with bases, compounds, which are much oftener the subject of analytical research than the acid itself, because these compounds are employed in several manufactures. They are very soluble in water, except chlorate of potash, which is difficultly soluble in this menstruum, though much less so than the perchlorate[1]; * wherefore, perchloric acid produces in a concentrated solution of chlorate of potash an abundant precipitate of perchlorate of potash. This chlorate is much more soluble in hot than in cold water.

* Except chlorate of potash, of soda, of ammonia, of baryta, strontia, protoxyde of lead, and oxyde of silver, all the other chlorates deliquesce in the air.

The great solubility of the chlorates prevents chloric acid from being precipitated from their solutions in the state of chlorate by a base, or by the solutions of other salts. A concentrated solution of potash, or of a salt of potash only, can precipitate chloric acid in the state of chlorate of potash when poured in the concentrated solutions of the soluble chlorates. This is also the reason why the solutions of pure chlorates are not precipitated by nitrate of silver. But when these salts have not been prepared directly by saturating the pure acid with bases, they frequently contain metallic chlorides, which it is sometimes difficult to eliminate, and owing to their presence, solution of nitrate of silver often produces a precipitate in their solutions. Solutions of pure chlorates have no action upon litmus paper. * All the compounds of chloric acid with bases are neutral.

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[1] According to Gay Lussac, 100 parts of water at 32° Fahr. dissolve 3·5 parts of chlorate of potash; at 59°, 6 parts; at 95°, 12 parts; at 120°, 19 parts; at 216°, a temperature at which the saturated solution boils, 60 parts, whilst the perchlorate requires more than 50 parts of water at 60° to dissolve one part.—ED.

When the dry compounds of chloric acid, with alkalies, alkaline earths, and other powerful bases are exposed to a red heat, oxygen is disengaged, and they are converted into metallic chlorides, and perchlorates; * the latter product being exposed to a still stronger heat, undergoes a further decomposition, producing a disengagement of oxygen gas, and ultimately nothing remains but metallic chlorides. It is sufficient to heat by means of the spirit lamp a small quantity of a chlorate introduced into a tube closed at one end to be convinced that oxygen gas is disengaged, for a glimmering match held at the orifice of the tube is immediately kindled and burns with characteristic vividness. If the residuum of the ignition of the salt be dissolved in water, the addition of nitrate of silver gives an abundant precipitate of chloride of silver.

When concentrated SULPHURIC ACID, in the cold, is poured upon a chlorate placed in an open vessel, for example, in a somewhat large tube of white glass, closed at one end, there is a disengagement of greenish-yellow vapours of chlorous acid analogous to the colour of chlorine, but a little deeper. It is necessary, in such an experiment, to operate only on small quantities of the salt and not to heat the mixture, because otherwise an explosion would take place. The chlorate is thereby converted into a bisulphate and a perchlorate.

When a little dilute MURIATIC ACID is poured upon chlorates, and the whole cautiously heated, greenish-yellow vapours of chlorine are evolved[1].

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[1] Not of chlorine, but chiefly of protoxyde of chlorine mixed with chlorine. This gas is highly explosive, the heat of the hand being often sufficient to cause detonation.—ED.

When chlorates, especially those which contain no water of crystallisation, are heated in conjunction with sulphur, carbon or substances containing carbon, such as sugar, with some metals and metallic sulphurets, but especially with phosphorus they detonate most violently, in consequence of which, such experiments should be carried on with extreme caution, and only on small quantities at a time. When the chlorates are mixed with sulphur or cinnabar, but more especially with phosphorus, it is sufficient to strike them with a hammer on an anvil to produce a detonation. This effect is produced also by a blow with the pestle in a metallic mortar. When a mixture of chlorate and of sulphur is moistened with fuming sulphuric acid, it bursts into flame. Ignition is not always produced when ordinary oil of vitriol is employed, but these substances always react powerfully upon each other, and there is an odour of chloride of sulphur emitted[1].

The chlorates are easily recognised by the violent detonations which they produce, when heated in contact with organic bodies; * and also, because most of them (and these are the most important) are converted into oxygen and a metallic chloride by the action of a red heat.

* In the dry state, or in solution, they are distinguished from the perchlorates, because the latter are not altered by sulphuric nor by muriatic acid, whilst the chlorates by the action of sulphuric acid are decomposed, become yellow, and disengage a greenish-yellow gas.

They differ from the nitrates and nitrites, because the gas disengaged by these, when treated by sulphuric acid, is ruddy, and does not smell like chlorine.

* Pure chloric acid is distinguished from perchloric acid, because the latter acid is not decomposed by muriatic, nor by sulphurous acids, sulphuretted hydrogen, nor alcohol[2].

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[1] A mixture of a chlorate and cyanide of potassium heated in a platinum crucible detonates violently, even though there be only a very minute quantity of chlorate. Only very small quantities should be operated upon.—Ed.

[2] Chloric acid in a free state, and consequently the solution of chlorates when

* The following note, by M. E. Peligot, is met with in the French edition:—

M. Millon has lately discovered a new combination of chlorine and oxygen, composed of one equivalent of chlorine, and three equivalents of oxygen ClO_3, corresponding consequently to nitrous acid; but the name of chlorous acid, which M. Millon has given to the compound, cannot be retained here, since M. H. Rose calls by that name the acid discovered by M. Balard. We shall call it, therefore, HYPOCHLORIC ACID, and under that name briefly indicate its principal characters.

* When the compound of chlorine and oxygen ClO_4, generally called deutoxyde of chlorine, is put in contact with an alkali, it generally behaves like hyponitric acid, to which it corresponds; the result being a mixture of chlorate, ClO_5 RO, and of hypochlorite ClO_3 RO; it is known that the deutoxyde of chlorine gas is of an intense yellow colour, which spontaneously detonates with great violence, even at the ordinary temperature; it is prepared by cautiously treating chlorate of potash by sulphuric acid, diluted with about half its weight of water.

* Hypochloric acid is likewise produced, according to M. Millon, by deoxydising chloric acid, provided the operator remains within the limits of the temperature, beyond which it is destroyed. It may, for example, be prepared in the gaseous state, by submitting to a temperature of about 50° cent. (122° Fahr.), a mixture of chlorate of potash, of tartaric acid, and of diluted nitric acid; carbonic acid is disengaged at the same time.

* Hypochloric acid is a very deep greenish-yellow gas; its odour very much resembles that of deutoxyde of chlorine. It

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treated by sulphuric acid, decolorise indigo exactly as nitric acid, especially by heating the mixture to the boiling point, as has been said in the article on nitric acid and the nitrates. When therefore this test is resorted to for the detection of chloric acid, the absence of nitric acid or of a nitrate must be ascertained beforehand. Dr. Fresenius remarks, that if to the liquid under examination, a few drops of solution of sulphate of indigo be added, so as to render it slightly blue, a solution of sulphurous acid poured carefully therein decolorises the indigo, owing to the sulphurous acid depriving the chloric acid of its oxygen, and thus liberating chlorine, which then reacts upon the indigo.—ED.

bleaches litmus paper and sulphate of indigo. At about 60° cent. (140° Fahr.) it is decomposed with a slight explosion.

* Water dissolves about five or six times its bulk of this gas, and assumes at the same time a very deep golden tinge; a single bubble is sufficient to impart a greenish-yellow colour to a quart of water[1].

* The aqueous solution of hypochloric acid acts variously upon metals; with mercury it forms a perchloride; with copper, a mixture of chlorate and of chloride; with zinc and lead, a mixture of chlorite and of chlorate. It does not attack antimony[2].

* All oxydes without exception, even the alkaline ones, combine with difficulty with this acid; hydrate of lime has no action upon gaseous hypochloric acid, and even potash combines but slowly, and only after a prolonged agitation.

* Hypochlorates of lead, of silver, of baryta, and of strontia, have been obtained in crystals in a pure state; treated by dilute nitric acid they disengage hypochloric acid in the gaseous state.

* Hypochloric acid gas may be distinguished from chlorine, because its bleaching power is not destroyed by a solution of arsenious acid in muriatic acid; it continues to act upon sulphate of indigo, however large may be the quantity of arsenious acid present. It differs from deutoxyde of chlorine, because, when treated with potash, it does not form a chlorate.—E. P.

3°. CHLOROUS ACID, ClO.

(Acide Chloreux.)

* ACCORDING to Balard, the aqueous solution of chlorous acid, when it has been obtained by causing chlorine gas to be absorbed by a mixture of protoxyde of mercury and water,

is a transparent liquid which, when concentrated, has a slightly yellowish colour. This acid has a penetrating odour differing greatly from that of chlorine, and a strong, but not an acid taste. It decomposes most organic substances with disengagement of carbonic acid gas, and of gaseous chlorine; it converts indigo into a yellow, slightly bitter substance. It strongly attacks the epidermis, and tinges it brownish-red. It is easily decomposed, especially in the concentrated state, chlorine gas is evolved, and it is converted into chloric acid. At the temperature of boiling water, this decomposition is only slight, so that this acid may be distilled, and concentrated by means of the water bath.

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[1] Solar light decomposes hypochloric acid gas and the solution thereof.—ED.

[2] M. Millon says that gold and platinum also resist its action. Dry hypochloric acid gas does not act upon metals, even upon zinc. Metallic mercury alone absorbs it without residuum.—ED.

* Chlorous acid is gaseous; its yellow colour resembles that of chlorine, with which, in this respect, it might easily be confounded. Its odour is analogous to that of the aqueous solution. It is absorbed by water and by mercury. At a high temperature it detonates, and is decomposed into chlorine and oxygen gases. Muriatic acid transforms it into chlorine and water. It converts metallic chlorides into oxydes and perchlorides. It acidifies bromine, iodine, sulphur, selenium, phosphorus, and arsenic; the two first substances without, and the four last with, detonation and liberation of chlorine which combines with the excess of the substance.

* The aqueous acid combines with the powerful bases, especially with the alkalies and alkaline earths; yet the chlorites thus produced are easily decomposed. They resist decomposition for a longer time when they contain an excess of base, and in that case they may at a low temperature be evaporated to dryness in vacuo. At a somewhat high temperature they are converted into chlorates, and metallic chlorides, which conversion is often accompanied with a slight disengagement of oxygen gas, when the base is in excess.

* These chlorites are identical with the combinations obtained by passing chlorine gas through diluted solutions of pure alkalies, or alkaline carbonates, or through hydrate of lime; the only difference consists in this, that the latter combinations are

mixed with the corresponding metallic chlorides. In a practical point of view, these combinations are exceedingly important, and doubtless they are much oftener the subject of analytical investigation than the pure chlorites. Many chemists have considered them as compounds of chlorine, and of the basic oxydes by which they are produced, whence they are generally known under the name of chloride of potash, chloride of soda, chloride of lime, denominations which we shall retain here for the sake of brevity.

* Chloride of potash and chloride of soda are completely soluble in water; chloride of lime when treated by water leaves a residuum of hydrate of lime. These solutions have a peculiar taste, similar to that of the aqueous solution of chlorous acid; and they differ from the combinations which chloric and perchloric acid form with bases, because they destroy the colour of litmus paper and other organic colours; even indigo is easily destroyed by them; yet this effect is ordinarily produced only when a dilute acid is further added.

* If an excess of dilute muriatic, sulphuric, or other acids, even nitric acid, be added to the solutions of these combinations, chlorine gas is evolved, and the odour of putrefying animal matter is thus destroyed. Vinegar and other vegetable acids likewise disengage chlorine from these solutions, but with less energy. The carbonic acid of the air is even sufficient gradually to determine this disengagement, so that, like the same combinations in the solid state, they disengage a feeble odour of chlorine and are converted into carbonates when abandoned for a long time in contact with the air.

* If a current of carbonic acid gas be passed through a solution of chloride of alkali, chlorine is more rapidly disengaged.

* The chlorine gas which acids disengage from chlorides of alkalies generally contain a small quantity of chlorous acid.

* Concentrated phosphoric acid put in contact with pure chlorites completely free from the corresponding metallic chlorides, expels chlorous acid gas, which is, however, difficult to obtain completely free from chlorine gas.

* A very small quantity of solution of **NITRATE OF SILVER** poured in solutions of chlorides of potash, of soda, or of lime, produces a white precipitate of chloride of silver, because they contain some metallic chloride. If a larger quantity of nitrate of silver is employed, a black precipitate is formed, produced by the excess of base which these solutions contain; and when nitric acid is added to this black precipitate it is converted into a white curdy precipitate of chloride of silver.

* When in these solutions an excess of one of nitrate of lead is added, a precipitate is formed which is white at first, but which soon turns yellow. The filtered liquor deposits in time some peroxyde of lead.

* Submitted to evaporation the solutions of chlorides of alkalies are gradually decomposed, exactly like the pure chlorites, into metallic chlorides and chlorates.

* When these combinations are heated in the solid state in a retort over the spirit-lamp, a small quantity of chlorine is at first disengaged, and the chlorites are converted into *metallic* chlorides and chlorates; the latter, if the application of heat be continued, are likewise converted into metallic chlorides and into oxygen which escapes in the gaseous state, and is easily recognised as such by the property which it possesses of rekindling a glimmering splinter held at the orifice of the neck of the retort.

* The disengagement of gaseous chlorine, which takes place when the solutions of the combinations of chlorites with metallic chlorides are treated with dilute acids, and that of oxygen produced by heating them, are two characters which distinguish these from all other combinations.

In the French edition the following remarks by E. Peligot have been added:—

According to the recent researches of M. Gay Lussac, chlorous acid is easily prepared by putting in contact chlorine and oxyde of mercury both well dried, into a stoppered glass bottle of about fifty or sixty cubic inches capacity, full of chlorine; a glass tube closed at one end is introduced, the two-thirds of which tube are filled with oxyde of mercury, and the remaining third contains fine well-dried sand. The tube is placed in the bottle, with the closed end downwards, and after having fixed the stopper, which is slightly greased, the sand and the oxyde of mercury are gently shaken out; the colour of the chlorine almost immediately vanishes, and the experiment is complete. On opening the bottle under mercury, it (the mercury) rises in it about half way up; with water the absorption is very rapid and almost entire.

* M. Balard has attributed to chlorous acid gas a yellow colour more intense than that of chlorine. M. Gay Lussac has always obtained it perfectly colourless, even in aqueous and in alkaline solutions, which contain more than twenty times their bulk of it.

* The predominating character of this acid is, that it is very unstable; in the gaseous state it sometimes explodes at the ordinary temperature; dissolved in water it is more fixed, yet it gradually undergoes spontaneous decomposition. Solar light greatly accelerates its decomposition, especially when concentrated.

* A given volume of chlorous gas containing an equal bulk of chlorine and half a volume of oxygen, these two bodies having exactly in the acid the same decolorising power, the result is, that the power of a solution of chlorous acid must be referred for one half to the chlorine, and the other half to the oxygen.

* M. Gay Lussac has established, by decisive experiments, that the combinations formed by chlorous acid and the bases cannot be assimilated by their composition to hyposulphites and hypophosphites, and that their true formula, calling R the metallic radical, is ClO, RO, and not Cl_2O_3, RO''; this last formula was generally admitted, as is well known.

* When a chlorite mixed with a metallic chloride in sufficient quantity is treated by an excess of sulphuric acid, chlorine

is immediately evolved with effervescence. The metal of the chloride takes up the oxygen of the chlorous acid, and dissolves in the sulphuric acid, and the chlorine furnished both by the chloride and by the acid is set free and is disengaged.

* But if the sulphuric acid is added with care, and at most in just sufficient quantity to decompose the chlorite only, chlorous acid, not chlorine, is then disengaged; this important observation of M. Gay Lussac permits the employment of chlorides of oxydes for the preparation of chlorous acid. These compounds in effect are mixtures of chlorites and of chlorides; thus the neutral chloride of potash, ClO, KO, produced by the action of chlorine upon a dilute solution of caustic or carbonated potash, behaves like a mixture of ClK + ClO, KO; treated by a quantity of sulphuric acid sufficient to saturate only half the potash employed to produce it, it furnishes chlorous acid in the state of a colourless solution, from which it may easily be separated by distilling the liquid at a gentle heat.—E. P.

6. BROMIC ACID, BrO_5.

(*Acide Bromique.*)

Aqueous bromic acid is a colourless or slightly reddish liquid which, with proper care may like chloric acid be evaporated to syrupy consistence, but it cannot be distilled without undergoing a decomposition, the result of which is, that part of it is converted into bromine and oxygen gas. It reddens litmus paper, but when left for a long time in contact with it, it ultimately bleaches it. It is decomposed by muriatic, hydrobromic, sulphurous acids, and sulphuretted hydrogen[1] precisely as chloric acid.

* It is also very rapidly decomposed by alcohol and ether, much heat being disengaged, and there is a production of bromine and of acetic acid, part of which latter substance uniting

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[1] Bromic acid is also decomposed by phosphorous acid and by all the hydracids, bromine being reduced.—Ed.

with the portion of alcohol which has resisted decomposition, forms acetic ether.

Some bases which by combining with chloric acid form salts which are soluble in water, produce with bromic acid compounds some of which are sparingly soluble, others insoluble in that menstruum. Solution of NITRATE OF SILVER produces in solutions of bromates, even when free from metallic bromides, a white precipitate of bromide of silver, soluble in ammonia and insoluble in nitric acid. This precipitate may be distinguished from chloride of silver because it is only slightly blackened by the influence of daylight, and detonates like the bromates in general when, being mixed with pulverised charcoal, heat is applied.

A concentrated solution of NITRATE OF LEAD likewise gives a white precipitate in solutions of bromates; but this precipitate is redissolved by a large addition of water.

When bromates in the solid state are exposed to a red heat, they behave like the chlorates, that is to say, they are converted into metallic bromides, during the formation of which oxygen gas is evolved, which may be recognised as such by means which will be described further on. When mixed with charcoal, sulphur, or other combustible bodies, and heated, they detonate almost as violently as the chlorates; even percussion is often sufficient to produce this effect. If the mixture be moistened with fuming sulphuric acid it immediately bursts into flame. If the bromate contains water of crystallisation, the phenomena are less evident.

When bromates are introduced into a glass tube closed at one end, and concentrated SULPHURIC ACID is poured upon them, in the cold, gaseous bromine is disengaged, which is recognisable by its hyacinth-red colour. Oxygen gas is also evolved at the same time. Most bromates are decomposed in the same manner by nitric acid as well as by sulphuric acid, when, after having dissolved them in a small quantity of water, either of these two acids is added and the whole heated; the mixture becomes then altogether of a fine hyacinth-red colour, which is due to a liberation of bromine. Certain bromates, for example the bromate of baryta, are thus decomposed only in the solid state, but not when in solution.

Bromates have the greatest resemblance with chlorates. They are distinguished from them because solution of nitrate of silver produces in bromates a white precipitate, and because, in the solid state, they disengage, when treated by cold concentrated sulphuric acid, not a greenish-yellow gas like the chlorates, but a hyacinth-red gas somewhat resembling the colour of nitrous acid. The bromates differ from the nitrites by the manner in which they are decomposed when exposed to a red heat. They are distinguished from the other salts because, when mixed with combustible bodies and heated, they detonate violently.

* The existence of a *bromous acid*, BrO, is very probable, but has not yet been positively demonstrated.

7. ACIDS OF IODINE.

1°. OXYIODIC ACID, IO_7.

(Acide Oxyiodique.)

* According to Magnus and Ammermüller, aqueous oxyiodic acid is obtained by treating the neutral oxyiodate of silver by water, which extracts half the acid and leaves a basic oxyiodate of silver undissolved. The acid may be crystallised by a gentle evaporation. In the crystalline state it does not undergo any change in the air, nor does it deliquesce. When heated it is transformed first into oxygen gas and iodic acid, which in its turn is resolved into oxygen gas and iodine. The aqueous solution of the acid may be boiled without being decomposed. Muriatic acid decomposes it under disengagement of chlorine gas.

* According to Bengieser, oxyiodic acid fuses at 130° cent. (266° Fahr.), without decomposition; at 160° cent. (320° Fahr.) it loses its water of crystallisation; between 188° and 190° cent. (370° or 374° Fahr.) it is converted into iodic acid and oxygen. The crystallised acid is pretty soluble in alcohol and in ether. These solutions when dilute do not appear to undergo any change, even by boiling. Most metals are oxydised by the aqueous acid.

* The solutions of the neutral salts of baryta, of lime, of protoxyde of lead, added to a solution of oxyiodic acid, perfectly saturated with carbonate of soda, precipitate therefrom insoluble basic oxyiodates of a white colour, and the filtered liquid reacts like an acid. If the oxyiodate of lead be heated, or if it be precipitated from a warm solution of oxyiodic acid, it is yellow, and contains no water of crystallisation. The same phenomena are produced with the subsalts and protosalts of mercury. When subnitrate of mercury is poured in a solution of neutral oxyiodate of soda a yellow precipitate is produced, which becomes brownish-red by applying heat. With the solution of a protosalt of mercury (for example, corrosive sublimate) a white precipitate is obtained, which heat renders yellowish; with a solution of protoxyde of copper a yellowish-green precipitate, which becomes deeper by warming; salts of proto and of peroxyde of iron produce a whitish-yellow precipitate. All these precipitates are easily soluble in dilute nitric acid.

* Oxyiodic acid forms with alkalies as with oxyde of silver, neutral and basic salts. The two salts of potash are very sparingly soluble, like the oxychlorate of that base. The neutral oxyiodate of soda is very soluble, and the basic oxyiodate of soda is almost insoluble. The neutral oxyiodate of silver has an orange colour, and is decomposed by water; and the basic salt which is thereby produced is insoluble in that liquid. This basic salt is yellow, and assumes a brownish-red colour after treatment with hot water; it then contains less water than the yellow salt. Basic oxyiodate of silver is precipitated even from the solutions of neutral or basic alkaline oxyiodates to which water has been added, when a solution of nitrate of silver is subsequently poured in. This character may serve to detect oxyiodic acid in these liquids.

* Oxyiodates are decomposed by exposure to a red heat under disengagement of oxygen gas; the neutral oxyiodates leave a residuum of metallic iodide; the basic oxyiodates leave a mixture of metallic iodide and of oxyde, or if the latter be reducible by heat, such as, for example, oxyde of silver, the residuum is a mixture of iodide and of metal. The basic

oxyiodate of soda abandons three-fourths of its oxygen at a heat which glass can bear: it is necessary to increase the heat considerably in order to expel the last fourth part. The mass, which has been feebly heated to redness, and which is next dissolved in water, gradually decolorises litmus paper.

2°. IODIC ACID, IO_5.

(*Acide Iodique.*)

According to Sérullas, aqueous iodic acid may easily be obtained in crystals[1]. It is very soluble in water, but sparingly so in alcohol, by which, however, it is not materially decomposed. Exposed to the air it undergoes no change, though if the air be damp it deliquesces. At a high temperature it fuses, and is reduced into iodine and oxygen gas without residuum.

The aqueous solution of this acid reddens litmus paper in a permanent manner, according to Connel. * Several other vegetable colours are likewise reddened by it, but they do not retain that hue, and after a time become bleached. The solution oxydises the metals, even gold.

* MURIATIC ACID decomposes iodic acid, and when poured in a solution of the latter acid a strong odour of chlorine is immediately disengaged.

* SULPHURETTED HYDROGEN also decomposes iodic acid. When solution of SULPHURETTED HYDROGEN is poured in that of iodic acid a brown precipitate of iodine is formed, which is re-dissolved by addition of a larger quantity of liquid sulphuretted hydrogen, and sulphur is separated.

* A small quantity of SULPHUROUS ACID added to iodic acid determines a precipitate of iodine, insoluble in an excess of the re-agent[2].

* Iodic acid forms neutral salts with the bases, but with some of them it forms acid salts; such is the case, for example, with

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[1] Crystallised iodic acid, according to M. Millon, contains one atom of water.—ED.

[2] The sulphurous acid becomes converted into sulphuric acid, according to M. Millon. If iodic acid be dissolved in concentrated but not absolute alcohol, and sulphuric acid be poured in drop by drop, taking care that the mixture does not become too hot, white, shining, crystalline spangles are obtained on cooling, which are $HO+I_3O_8$. This combination may also be obtained with anhydrous alcohol.—ED.

potash. Most iodates are sparingly soluble, or insoluble, except the neutral iodates of alkalies, which are very soluble. Wherefore crystalline precipitates are produced when the solution of the iodate of an alkali is poured in that of a salt of baryta, strontia, lime, protoxyde of lead, or oxyde of silver.

* The precipitates which are formed in solutions of salts of baryta, protoxyde of lead, oxyde of silver, appear immediately; those formed in solutions or salts of strontia, and of lime, are manifested only after some time, and only when the liquids are concentrated (pages 26, 31, 36). The iodate of silver precipitated by a solution of nitrate of silver is soluble in ammonia, but, like the bromate of silver, it is not soluble in dilute nitric acid.

Sulphuric acid and other oxacids do not appear to have any other action upon the iodates, except to convert them into acid iodates, or else to separate the iodic acid.

When the iodates are mixed and heated with combustible substances they detonate, but not so strongly as the chlorates and bromates.

When the iodates are exposed to a red heat in a small retort, they are converted into metallic iodides under disengagement of oxygen. If the salt thus treated be an acid iodate, oxygen gas and vapours of iodine are disengaged, and the residuum is a metallic iodide.

The best character for detecting the iodates is the disengagement of oxygen and their conversion into metallic iodides when they are heated in a small retort. The disengaged gas may be recognised as oxygen by presenting to the orifice of the retort a glowing match, which is immediately rekindled. I shall indicate further on, when treating of metallic iodides, how a metallic iodide, or rather iodine in a metallic iodide, can be detected.

8. ACIDS OF PHOSPHORUS.

1°. PHOSPHORIC ACID, PhO_5.

(*Acide Phosphorique.*)

Phosphoric acid is obtained in the anhydrous state by burning phosphorus in a great quantity of oxygen, or of dry atmospheric air; it is then in the form of white flakes. Aqueous phosphoric acid (hydrated) may be obtained in the solid state by evaporating its aqueous solution in platinum vessels, heating the residuum for a long time by a gentle fire, in a covered platinum crucible, and finally exposing it to a red heat; it then forms a nitrous mass, which deliquesces in the air, and is thus converted into a syrupy liquid[1]. If the ignited phosphoric acid be suffered to cool, and water be then poured upon it, it dissolves therein with a crackling noise which lasts some considerable time. When it has not been heated long enough in the covered platinum crucible, it forms, after cooling, a soft, viscid mass. When the phosphoric acid, which has a syrupy consistence, is heated in an open platinum crucible, it volatilises, producing thick white fumes, and if perfectly pure no residuum is left. The less pure phosphoric acid is, the less it is volatilised by heat, and the less also does it deliquesce in the air after cooling. Wherefore, when a phosphoric acid which is exposed to a red heat in open platinum vessels does not smoke at all, and produces, after a long lapse of time, a glass which is not deliquescent, which dissolves sparingly or not at all in water, we may conclude that it is mixed with a pretty large quantity of fixed foreign matter, and the glass in such a case contains no water.

Phosphoric acid attacks so strongly vessels of porcelain, and still more so those of glass, when melted therein, that it is thereby rendered less volatile and less deliquescent, and that afterwards it is no longer completely soluble in water. In the pure state this acid is very soluble in water, and also in alcohol.

* Phosphoric acid is detected in a solution by the same re-agents which indicate the presence of phosphates.

Phosphoric acid forms basic salts, amongst which, in the neutral state, those only are soluble in water which contain an alkali combined with the acid. The neutral combinations of phosphoric acid with the earths and metallic oxydes are insoluble in water, and dissolve only in an excess of phosphoric acid, or of another free acid. Several acid phosphates however, especially those of potash or of soda, after ignition, are insoluble in most acids, and dissolve in water only after boiling with concentrated sulphuric acid, provided always that they do not contain a base capable of forming with this acid a combination insoluble in water and in free acids.

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[1] Hydrate of phosphoric acid contains three atoms of water, $PhO_5 + 3\ HO$ (called by Professor Graham tribasic phosphate of water), and it is changed by heat into hydrate of pyrophosphoric acid (bibasic phosphate of water) if one equivalent of water be expelled, and into metaphosphoric acid (protohydrate of phosphate of water) if two equivalents of water be expelled.—Ed.

The neutral solutions of all the earths and metallic oxydes determine a precipitate in the neutral solutions of phosphates of alkalies. These precipitates are soluble in the free acids, and re-appear in the state of phosphates by saturating the acid with an alkali. Yet an excess of alkali, especially of potash, often deprives the salt of a portion of its phosphoric acid, and it is not possible by this means to deprive the precipitate of all its phosphoric acid. When the base of the precipitated phosphate is soluble in an excess of alkali, the phosphate is likewise soluble. In this respect phosphoric acid has the greatest analogy with other acids, forming with alkalies salts which are soluble in water, and with the earths and metallic oxydes, salts which are insoluble in water. * Yet when ammonia is employed to precipitate a phosphate from its acid solution, this salt is completely precipitated, though in some cases it is completely dissolved by an excess of ammonia, even though the base may be insoluble in this alkali, when uncombined with phosphoric acid. This is especially the case when the base of the phosphate is very weak, for example, peroxyde of iron (page 89).

The solutions of neutral phosphates of alkalies, therefore, produce precipitates not only with solutions of CHLORIDE OF BARIUM, OF CALCIUM, and of other soluble earthy salts, but likewise with LIME and BARYTA WATER. These precipitates are soluble in muriatic and in nitric acids; but the solutions of salts of ammonia, especially that of muriate of ammonia, dissolve them also, particularly that of phosphate of lime[1]. A considerable quantity, however, of the salts of ammonia is necessary to render the solution complete, and besides, almost the whole of the phosphate is reprecipitated from such a solution by free ammonia. Phosphate of lime and phosphate of baryta are likewise reprecipitated from such a solution by ammonia.

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[1] Phosphate of baryta is difficultly soluble in solution of sal ammoniac.—ED.

* The solution of a SALT OF MAGNESIA produces also a precipitation in that of a neutral phosphate of alkali, particularly by boiling the whole (page 40). By adding ammonia, or a solution of carbonate of ammonia, an insoluble basic ammonio-magnesian phosphate is precipitated, which is insoluble in solutions of ammoniacal salts[1]; wherefore, in certain cases, especially when the solution contains sulphuric acid at the same time, a solution of a magnesian salt is preferable to that of salts of lime or of baryta, to detect phosphoric acid[2].

The white precipitate which a solution of ACETATE or of NITRATE OF LEAD produces in the solution of phosphate of alkali, is almost insoluble in free acetic acid, but it dissolves in nitric acid. When this precipitate of phosphate of lead is dried and then fused upon charcoal in the exterior flame of the blow-pipe, the fused bead distinctly crystallises on cooling.

A solution of NITRATE OF SILVER produces a yellow precipitate in those of neutral phosphates of alkalies. Of all the precipitates which phosphoric acid determines, this is the most characteristic; for all the acids which have much analogy with phosphoric acid, form, with the exception of arsenious acid, precipitates of a different colour with oxyde of silver[3]. Even when the solutions of the phosphate and of the nitrate of silver employed are neutral, the supernatant liquid above the yellow precipitate reddens litmus paper, because the precipitate is a basic salt. The yellow precipitate of phosphate of silver is soluble in nitric acid and in ammonia, but it is not insoluble in a liquor which contains nitrate of ammonia, wherefore no precipitate can be produced in the solution of a very small quantity of pure phosphate of silver by a large quantity of nitric acid, when ammonia is cautiously added to the liquor so as to saturate it.

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[1] This precipitate is readily soluble in acids, even acetic acid.—ED.

[2] Free ammonia or its carbonate is generally added, because the test is thus rendered much more delicate in effect; in order to obtain a precipitate in solution of phosphates by the magnesian sulphate or chloride, the solution of the neutral phosphate must be somewhat concentrated, whilst, if free ammonia be added, as just said, and the mixture be stirred, a precipitate of ammonio-magnesian phosphate is thrown down in even very dilute solutions. This precipitate requires often some time and agitation to determine its production and separation.—ED.

[3] Mr. Parnell observes, that the solution of nitrate of silver likewise produces a yellow precipitate in solutions of alkaline silicates, which precipitate resembles phosphate of silver, not merely in colour, but likewise in solubility in acids and in ammonia. Before applying nitrate of silver, therefore, as the test for phosphoric acid, the absence of silicic acid should be ascertained in the usual way.—ED.

* A proof that the yellow precipitate of phosphate of silver is not dissolved by small quantities of nitric acid, is, that it can subsist, as we have just said, in a solution which contains a little free nitric acid. But it is produced when a solution of nitrate of silver is poured in a solution of pure phosphoric acid. A white precipitate is likewise manifested when the solution of phosphoric acid recently ignited, is mixed with nitrate of silver.

* It should be observed, however, that a white precipitate of neutral phosphate of silver appears, when a solution of nitrate of silver is poured in a solution of phosphate of soda which has previously been strongly ignited. This same white precipitate of neutral phosphate of silver is produced also when a recently prepared solution of ignited phosphoric acid, especially after saturation with an alkali, is poured in a solution of nitrate of silver. The solution of ignited phosphate of soda does not lose the property of giving a white precipitate with solution of nitrate of silver, however long it may be kept; but the solution of ignited phosphoric acid produces this reaction only when recent. The longer it is kept, the larger also is the quantity of yellow phosphate of silver precipitated by the solution of nitrate of silver. If, therefore, a recently prepared solution of ignited phosphoric acid be left at rest for a long time, it yields a mixture of white and of yellow precipitate when treated by solution of nitrate of silver.

Phosphoric acid, the phosphates, and acid phosphates soluble in water, are not precipitated nor converted into the inferior degrees of oxydisement of phosphorus by sulphuretted hydrogen, sulphurous acid, or other re-agents.

It sometimes occurs that the presence of phosphoric acid in the phosphates, which are insoluble in water, is overlooked, especially when the combinations which contain such phosphates are very complex, and when, besides phosphoric acid, other acids are simultaneously present, which behave like phosphoric acid towards re-agents. In such cases extreme attention is required, otherwise even large proportions of phosphoric acid may actually evade detection.

If phosphoric acid is combined with baryta, strontia, lime, or magnesia, its presence may be recognised, because, after dissolving the compounds in muriatic acid, phosphoric acid is reprecipitated under the form of a white precipitate by supersaturating the acid solution with ammonia. It is, of course, necessary to have ascertained previously by other experiments that the solution contains no arsenic acid, no boracic acid, nor a metallic fluoride, nor certain organic acids. In effect, baryta, strontia, and lime are precipitated by ammonia from their solutions only when combined with phosphoric acid, boracic acid, arsenic acid, or certain organic acids, or when they are in the state of metallic fluorides. And magnesia, which cannot be precipitated from its solutions by ammonia, when there is a sufficient quantity of sal ammoniac, or of other salts of ammonia, is nevertheless precipitated by that alkali, when combined with phosphoric acid.

* The existence of phosphoric acid in these combinations, when the acids which have been just mentioned are known to be absent, is more securely detected by dissolving the compounds in the least possible quantity of nitric acid, adding to the solution some solution of nitrate of silver, and pouring into the whole the quantity of ammonia exactly necessary to saturate the free nitric acid. The yellow precipitate of phosphate of silver is thus determined. It is, however, necessary that the nitric acid solution of the compound be as concentrated as possible, and so take care not to put any excess of ammonia at the time of saturating it, otherwise the combination of the

phosphate would be precipitated, and the oxyde of silver dissolved. But even when the earthy phosphate has been precipitated by a large excess of ammonia, the precipitate still remains yellow for a long time in the cold, and the ammonia in such circumstances dissolves the phosphate of silver but slowly; if, on the contrary, heat be applied, the precipitate at once becomes white, and consists altogether of earthy phosphate. If the analyst is in possession of only such a small portion of the precipitate of earthy phosphate, as to be doubtful whether he will succeed in obtaining the yellow precipitate of phosphate of silver from the nitric acid solution of the earthy phosphate, it is at least necessary to test it with the blow-pipe in the manner described below.

* When *nitrate of silver* is employed for the purpose of detecting phosphoric acid in solutions which contain muriatic acid, it may be done without difficulty. If the liquor is neutral, it is to be rendered acid by adding thereto some nitric acid, and then an excess of the solution of nitrate of silver is to be added; the chloride of silver thus produced is to be separated by filtering, and ammonia is to be added until near saturation, when the yellow precipitate of phosphate of silver will appear.

The presence of phosphoric acid is much more difficult to detect when combined with alumina. Phosphate of alumina behaves towards most re-agents like pure alumina; the acid solution is also precipitated by ammonia; and the precipitate of phosphate of alumina is soluble in an excess of solution of pure potash, and in a free acid exactly like pure alumina. In order to detect the presence of phosphoric acid in phosphate of alumina, the latter is first to be dissolved in muriatic acid; a solution of pure potash is next to be added in sufficient quantity to redissolve completely the phosphate of alumina first precipitated, and then a solution of silicic acid in potash (*liquor silicum*) is to be added[1]. Alumina is thereby precipitated either immediately, or after a short time, under the form of an insoluble gelatinous mass, which is a combination of alumina with silica and potash. Into the liquor filtered therefrom a solution of chloride of calcium is now to be poured, which, if phosphoric acid be present, determines a precipitate of phosphate of lime. But it is better, especially if there is reason to fear that the potash employed contains a little carbonic acid, to put a very slight excess of muriatic acid in the alkaline liquor, to saturate the acid by a little ammonia, and then to add chloride of calcium.

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[1] The *liquor silicum* is bisilicate of potash, obtained by fusing together 1 part of silica and 2·5 of carbonate of potash; the carbonic acid is expelled, and a residuum of bisilicate of potash is left which is soluble in water. This solution may also be obtained by digesting gelatinous hydrate of silica in solution of potash.—ED.

* Phosphate of alumina may also be dissolved in nitric acid, and the alumina precipitated, as has been said, by silicate of potash. The liquor is then to be filtered, neutralised with nitric acid, and by means of a solution of acetate of lead the phosphoric acid may be precipitated in the state of phosphate of lead, which may be easily recognised as such by means of the blow-pipe.

* But the best and quickest method of detecting phosphoric acid in phosphate of alumina consists in dissolving the latter compound in the smallest possible quantity of nitric acid, to pour a solution of nitrate of silver in the liquor, and then to add exactly enough ammonia to saturate the free acid, when the yellow precipitate of phosphate of silver will appear.

When phosphoric acid is combined with metallic oxydes, which are precipitable by hydrosulphuret of ammonia from solutions saturated or supersaturated with ammonia, but which are not precipitable from an acid solution by sulphuretted hydrogen in the state of metallic sulphurets; that is to say, therefore, when phosphoric acid is combined with the oxydes of manganese, of iron, of cobalt, of zinc, of nickel, of uranium, the acid of the solution is to be supersaturated with ammonia, and then these oxydes may be precipitated from their acid solutions thus supersaturated, by means of hydrosulphuret of ammonia. The liquor is then to be filtered in order to separate the metallic sulphuret thus produced; muriatic acid is to be added to the filtered liquid, so as to render it slightly acid, and the whole is left to digest in a warm place, until the odour of sulphuretted hydrogen has vanished. The sulphur liberated by the decomposition of the excess of hydrosulphuret of ammonia previously poured in is to be separated by filtration, and the clear liquid is then to be saturated with ammonia: it is, however, better to add to the filtered liquid some carbonate of potash, but in such small quantity as to leave it slightly acid, so as sensibly to redden blue litmus paper; after this, the liquor may lie for a long time in a warm place, so that the carbonic acid may be disengaged as completely as possible; ammonia is then poured in sufficient quantity to render reddened litmus paper slightly blue; this done, a solution of chloride of barium, or better still a solution of chloride of calcium, is to be added to the liquor, by which a precipitate of phosphate of baryta, or of lime, is produced, if the liquor contained phosphoric acid; but, of course, the absence of arsenic and boracic acid, and of all trace of metallic fluoride, and of organic acids, must be positively ascertained beforehand. Carbonate of potash is preferable to ammonia for the purpose of saturating the liquor, because, as we have said above, the phosphates of lime and of baryta are slightly soluble in liquids which contain muriate of ammonia or other ammoniacal salts, wherefore it sometimes happens that chloride of barium or of calcium produce no precipitate in a liquor saturated with ammonia, when the phosphate under examination is in very small quantity.

* But the presence of phosphoric acid may be still more safely detected by using a solution of sulphate of magnesia. After having separated the liquor from the metallic sulphuret and from the excess of hydrosulphuret of ammonia, it is to be supersaturated with ammonia, and then a solution of sulphate of magnesia is to be poured into it, to which enough free ammonia or muriate of ammonia is added, completely to dissolve the precipitate of hydrate of magnesia produced. A precipitate of ammonio-magnesian subphosphate is formed, which is insoluble in solutions of ammoniacal salts. The use of sulphate of magnesia presents this great advantage, that the liquor may contain considerable quantities of muriate of ammonia and of sulphuric acid, without any objectionable influence being exercised by these

substances upon the precipitation of the ammonio-magnesian phosphate.

* If, however, we wish to detect the presence of phosphoric acid in the compound above mentioned, by means of nitrate of silver, it is necessary to dissolve the compound in nitric acid, to supersaturate the solution with ammonia, to precipitate the oxyde in the state of a metallic sulphuret by means of hydrosulphuret of ammonia, to filter the liquid, and to destroy therein by means of nitric acid the excess of the re-agent which has been employed to precipitate the oxyde in the state of metallic sulphuret. The liquor having been heated long enough, that is, until all smell of sulphuretted hydrogen has disappeared, solution of nitrate of silver is added, and likewise a quantity of ammonia precisely sufficient to saturate the free acid, and the yellow phosphate of silver is thus thrown down. If too much nitrate of ammonia has been formed in the liquor, and if at the same time the quantity of phosphate existing therein is very small, it often occurs that no precipitate of phosphate of silver is obtained; and besides, if the least trace of sulphuretted hydrogen has not been expelled from the liquor, some oxyde of silver may be precipitated in the state of black sulphuret of silver, a very minute quantity of which suffices considerably to alter the colour of the phosphate of silver.

When phosphoric acid is combined with a metallic oxyde which sulphuretted hydrogen is capable of precipitating from acid solutions in the state of metallic sulphuret, this re-agent may be employed to effect the precipitation; the liquid is then separated from the sulphuret thus produced by filtering, the clear liquid is heated to expel the sulphuretted hydrogen which it might hold in solution, and it is then submitted to the tests above described for the purpose of detecting the presence of phosphoric acid therein.

If the phosphoric acid is combined with a metallic oxyde which can neither be precipitated in the state of metallic sulphuret from its acid solutions by sulphuretted hydrogen, nor from its solutions saturated with ammonia by hydrosulphuret of ammonia, but which is insoluble in a solution of potash, the greatest part of the phosphoric acid may yet be separated from such an oxyde by dissolving the phosphate in the least possible quantity of acid, and boiling the solution with an excess of a solution of potash. By this process the oxyde is ordinarily precipitated with its characteristic colour, though in combination with a small quantity of phosphoric acid, the greatest part of which acid is, however, combined with potash in the solution filtered from the precipitated oxyde; and the phosphoric acid may then be detected in this filtered solution by the re-agents which have been indicated. The acids which behave towards re-agents in the same manner as phosphoric acid are likewise separated by this method from the base with which they were combined[1]. By this process the presence of phosphoric acid may be detected when combined with oxyde of chromium and protoxyde of cerium; and it is often a more speedy way than those which have already been exposed, of detecting phosphoric acid when combined with magnesia, protoxyde of manganese, the oxydes of iron, oxyde of nickel, and other bases.

* When a phosphate is combined with a sulphate, a circumstance of frequent occurrence, and when the bases of the salts are alkalies, so that the latter are soluble in water, the presence of the phosphoric acid may be detected by means of sulphate of magnesia; following the rules which have been set forth above, a precipitate of ammonio-magnesian phosphate is thus obtained.

In order to detect phosphoric acid in excessively minute quantities of phosphates, proceed as follows, according to Thénard and Vauquelin. A small portion of potassium or of sodium is to be introduced at the bottom of a glass tube closed at one end, and upon the potassium or sodium a small quantity of the substance which is undergoing examination for phosphoric acid is placed. Provided the substance is quite dry, one milligramme (·0154 grain) is sufficient for the purpose. The whole is then cautiously heated to redness, a temperature at which the potassium or the sodium reduces the phosphoric acid, and converts it into phosphuret of potassium or of sodium; the excess of potassium or of sodium is removed by means of a little mercury introduced in the tube and poured out again, and then by blowing cautiously with a small glass tube upon the mass at the bottom, so as to moisten it with the breath, it exhales a strong odour of phosphuretted hydrogen, which is quite characteristic[1].

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[1] It is therefore necessary that the analyst should first convince himself of the absence of these acids.—Ed.

Before the BLOW-PIPE the presence of phosphoric acid in the solid phosphates may be detected, according to Berzelius, in the following manner. A small portion of the substance under examination is fused upon charcoal with boracic acid, and when the swelling of the mass has ceased, a small piece of fine steel wire is forced through the bead so as to project on each side of the bead, and then the whole must be strongly heated in the interior flame. After cooling, the globule is removed from upon the charcoal, and, wrapping it in a piece of paper, it is deposited upon an anvil, and then gently struck with a hammer; by this means the separation of the phosphuret of iron produced is effected under the form of a round metallic grain, which is magnetic, brittle, and which flies to pieces when struck with a hard blow. This process, however, is insufficient to detect small quantities of phosphoric acid in the substance under examination. It is also necessary that the said substance should contain no sulphuric nor arsenic acid, nor any metallic oxyde capable of being reduced by iron, because in such a case a bead equally brittle, fusible, and in many respects similar to phosphuret of iron, is obtained. If, however, the substance has remained for a long time in fusion with the boracic acid, this acid will have displaced the sulphuric as well as the arsenic and arsenious acids. This method requires besides that the analyst should be expert in the management of the blow-pipe.

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[1] If a solution contains phosphoric acid, or a phosphate either of alkali or of metallic oxyde, it may be detected as follows:—Hydrochloric acid is to be added until the solution under examination reddens blue litmus paper, and to this acidified solution a few drops of perchloride of iron are to be added first, and afterwards a solution of ammonia, or, better still, of acetate of potash in excess, which determines a white pasty precipitate of perphosphate of iron, which, however, has a reddish colour when an excess of perchloride of iron has been employed; in which case, if solution of ammonia has been added, acetic acid is poured in to dissolve the uncombined peroxyde of iron, whilst the perphosphate of iron may be collected on a filter.—ED.

When a solid phosphate is moistened with sulphuric acid, and held between the platinum points of a forceps in the inner flame of the blow-pipe, the exterior flame acquires a greenish colour. This method of detecting phosphoric acid before the blow-pipe has been indicated by Fuchs. It gives a good result only in a small number of cases, and it must be remarked that borates produce similar phenomena.

The phosphates are not volatilisable by heat when the base combined with the phosphoric acid is of a fixed nature[1]. Most of them are fusible at a high temperature. This is principally the case with the acid phosphates, which, after fusion, become insoluble in most acids. A great number of these salts are decomposed by charcoal at a red heat; in certain instances a metallic phosphuret is formed, and in other instances, especially when the phosphoric acid is in excess, phosphorus sublimes.

From what has been said touching the behaviour of phosphoric acid towards re-agents, it is seen that the detection of this acid is often attended with very great difficulties. Phosphoric acid is recognised in a positive manner, because the absence of other acids, which react like phosphoric acid, may be clearly demonstrated in the compounds under examination. The property which phosphoric acid possesses of forming with protoxyde of lead a combination which, after fusion before the blow-pipe, crystallises on cooling, is the only reaction which is quite characteristic, as no other acid whatever possesses it. The behaviour of this acid and of the phosphates towards potassium is also a reaction which is quite characteristic. By these tests alone, therefore, can the compounds of phosphoric acid be detected from all other combinations.

As to the behaviour of phosphoric acid with *organic substances*, it is especially important to bear in mind the phenomena which it produces with a solution of albumen. A recently prepared solution of fused phosphoric acid leaves a precipitate in even a very dilute solution of albumen. The older the acid liquor is, the less does it possess this property of precipitating albumen from its solution; and it not only loses it altogether ultimately, but it acquires the power of re-dissolving coagulated albumen with the help of heat.

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[1] The fixed phosphates are not decomposed by heat, but they are thereby converted into pyrophosphate (bibasic phosphate of water), $PhO_5 + 2\,HO$, or into metaphosphates ($PhO_5 + HO$.)—Ed.

2°. PHOSPHOROUS ACID, PO_3.

(Acide Phosphoreux.)

* PHOSPHOROUS ACID may be obtained in the aqueous state, and as concentrated as possible, by decomposing the liquid protochloride of phosphorus by means of water, and cautiously evaporating the liquor. It then forms a thick syrupy liquid, which sometimes, but not always, may be obtained in crystals. It is very soluble, and in all proportions, in water; but the solution slowly absorbs oxygen, and is partially converted into phosphoric acid.

* When aqueous phosphorous acid as concentrated as possible is heated over a small spirit lamp in a small platinum spoon, or any other vessel, phosphuretted hydrogen is disengaged, which, owing to the action of the heat, burns with a greenish flame, and emits whitish fumes. If the acid be heated in a small retort, the phosphuretted hydrogen disengaged does not spontaneously ignite on coming in contact with the air; it has a very disagreeable smell, and when it is set fire to it burns with a vivid light, and emits white fumes at the same time. When the gas is passed through a solution of nitrate of silver, the smallest portion suffices to produce therein a brownish turbidness, and then a blackish-brown precipitate, which is metallic silver. The liquor afterwards contains phosphoric acid. Whenever liquid phosphorous acid is heated, either in a platinum spoon or in a retort, phosphoric acid remains. Phosphorous acid forms with the bases salts, amongst which those only are very soluble which are produced by combination with alkalies. The earthy and metallic phosphites are not all insoluble in this menstruum, but most of them dissolve only with great difficulty; but all the phosphites are soluble in free acids. By mixing the solution of an alkaline phosphite with a neutral solution of most earthy and metallic salts, precipitates are produced; yet these precipitates are ordinarily inconsiderable in the cold; but when the

mixture is heated, the greatest part, and sometimes the whole of the phosphorous acid, is precipitated. Very often the solutions of earthy and of metallic salts produce no precipitate in solutions of alkaline phosphites, when these solutions are too dilute; yet even in these a precipitate, which often is very large, may be determined by long standing, or by boiling. This peculiarity establishes quite a distinct difference between the phosphites and the corresponding phosphates.

* Of all the earthy phosphites, phosphite of magnesia is the most soluble[1]; wherefore no precipitate is obtained, even by boiling, when a solution of sulphate of magnesia is added to that of phosphite of alkali, provided the latter be not too concentrated. The phosphite of lead is probably the most insoluble of all the phosphites; wherefore it is always produced under the form of a white precipitate, when a solution of acetate of lead is poured in even very dilute solutions of phosphites[2].

* The solutions of phosphites in acids, like that of phosphorous acid itself, reduce several easily reducible metallic oxydes, a property which offers a good and characteristic mode of recognizing this acid. They precipitate gold in a metallic state from its solution. When these solutions are poured in one of NITRATE OF SILVER, the silver is precipitated under the form of a blackish-brown powder. When the solution of a phosphite, or that of phosphorous acid, contains muriatic acid, as is the case with the aqueous solution of liquid chloride of phosphorus, it is best to add an excess of ammonia, and then the solution of nitrate of silver. The liquid at first turns brown, and it is only after a long time that the blackish-brown precipitate of metallic silver settles. This result is obtained more rapidly by boiling, during which the precipitate becomes black. A solution of phosphorous acid poured in solution of PROTOCHLORIDE OF MERCURY (corrosive sublimate), provided too large a quantity be

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[1] Phosphite of magnesia, though more soluble in water than the other earthy phosphites, is very sparingly so, since 400 parts of water dissolve only one of this phosphite.—ED.

[2] Berzelius observes, that phosphite of lead is soluble in cold nitric acid, and is not thereby transformed into phosphoric acid.—ED.

not employed, produces a white precipitate of subchloride of mercury (calomel), insoluble in muriatic acid, and which augments by long standing; a larger proportion of phosphorous acid, especially by boiling, converts this precipitate into metallic mercury. An excess of solution of protochloride of mercury is therefore one of the best tests for the detection of phosphorous acid; for other substances which have a great reducing power (for example, sulphurous acid) do not produce any precipitate of subchloride of mercury in this solution. Subchloride of mercury besides is a substance which is easily recognised by its insolubility in muriatic acid. A solution of a protosalt of copper is likewise reduced by phosphorous acid, but to effect this the whole must be boiled.

* In the solid state, all the phosphites undergo decomposition by exposure to a red heat, and are converted into phosphates. During the operation most of them disengage hydrogen gas, because their water of crystallisation is decomposed, the oxygen of which transforms the phosphorous into phosphoric acid. Calcining converts the neutral phosphites into neutral phosphates. The combinations of phosphorous acid with the fixed alkalies, the earths, and many metallic oxydes belong to this category. The hydrogen gas disengaged contains very minute traces of phosphorus, and the phosphate which is produced contains also a small portion of that substance, which imparts to it a slightly reddish or brownish tinge, whilst when pure it is white. This colouring, produced by calcining the phosphate, does not appear until after cooling. If the salt be heated it becomes colourless, and if it be dissolved in muriatic acid a minute trace of a reddish substance which contains phosphorus is left as residuum. Other phosphites which contain less water of crystallisation are converted into basic phosphates by calcining, during which phosphuretted hydrogen gas, very poor in phosphorus, is disengaged, which does not spontaneously ignite in contact with the air, but which, being set fire to, burns vividly, and then emits white fumes. Such is the case, for example, with phosphite of lead.

* These experiments may be made with even a very small

quantity of phosphites, by heating them upon the spirit lamp in a glass tube closed at one end, and which has been drawn into a long point above the part where the salt lies. Phosphite of ammonia loses its ammonia when heated, and is converted into aqueous phosphorous acid.

* When a phosphite, or a concentrated solution of pure phosphorous acid, is mixed with a concentrated solution of pure potash, and the whole is boiled, no hydrogen is disengaged, and the phosphorous is not converted into phosphoric acid.

* Before the BLOW-PIPE, the phosphites might be distinguished from other combinations by the same method indicated by Berzelius for the phosphates (page 270). The first impression of the flame causes them to burn something like phosphorus.

* The behaviour of concentrated phosphorous acid is so characteristic when heated, and when it is made to react upon easily reducible metals, for example, protochloride of mercury, that it cannot be confounded with any of the acids hitherto treated of. The deportment of the phosphites when exposed to a red heat in a retort is likewise so remarkable, that they may be thus easily distinguished from other salts.

* The combination of phosphorous and of phosphoric acids, which is looked upon by many chemists as a distinct acid, and which they call *hypophosphoric acid,* is the result of the slow and spontaneous combustion of phosphorus in a moist atmosphere [such as by abandoning sticks of phosphorus in a funnel, by which means a sour liquid is gradually obtained[1]]. In a concentrated state it behaves, when heated, like phosphorous acid, because effectively it contains some of it. If this liquid be treated by the bases, it yields phosphates and phosphites.

* Phosphorous acid is easily detected in this combination, if in a very concentrated state, not only by heating it, but also, if

the liquid be dilute, by means of solution of protochloride of mercury. As to phosphoric acid, the best method to ascertain its presence is to add to the solution of the compound a solution of sulphate of magnesia, of sal ammoniac, and of excess of ammonia, and to put such a quantity of sal ammoniac as to prevent the precipitation of the magnesia by the ammonia. By this method the phosphorous acid is not precipitated, at least when its solution is a dilute one, whilst the phosphoric acid is thrown down in the state of ammonio-magnesian phosphate.

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[1] This sour liquid, obtained at the beginning of the operation, consists only of phosphorous acid, but as it remains in contact with the air it becomes oxydised, and is partially converted into phosphoric acid, so that ultimately it is nothing else but a mixture of the two acids, but not in definite proportions ; consequently, the name of hypophosphoric and of phosphatic acid, by which it is occasionally designed, is erroneous. The salifiable bases, saturated with this liquid, yield a mixture of phosphates and phosphites.—ED.

The following observation by Mons. E. Peligot is added in the French edition:—

* If phosphorous acid be mixed with an aqueous solution of sulphurous acid, an abundant precipitate of sulphur is immediately formed, and the phosphorous acid is thereby transformed into phosphoric acid: this reaction, observed by Wöhler, offers an excellent means of detecting the presence of phosphorous acid in phosphoric acid; if the latter acid contains arsenious acid at the same time, the precipitate turns yellow on account of the sulphuret of arsenic formed[1].

* Phosphorous acid may also be well detected by Marsh's apparatus, because phosphuretted hydrogen is thus produced, which is easily recognized by its garlick odour; and if the flame be depressed by a piece of china, a luminous circle may be observed, as when phosphorus burns in a confined atmosphere, or in chlorine.

3°. HYPOPHOSPHOROUS ACID, PhO.

(*Acide Hypophosphoreux.*)

* AQUEOUS hypophosphorous acid, in as concentrated a state as possible, resembles so much concentrated phosphorous acid by its behaviour towards re-agents, that it can hardly be distinguished from it. It has never yet been obtained in crystals. The solutions of gold and of protochloride of mercury are reduced

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[1] In order to detect the presence of phosphorous acid in phosphoric acid, Wöhler proceeds as follows:—Add to the solution under examination an aqueous solution of sulphurous acid, and expose the whole to a moderate heat. If phosphorous acid be present, sulphur will be separated; if arsenious or arsenic acid be also present, a yellow precipitate of sulphuret of arsenic is formed.—ED.

by it still more rapidly than by phosphorous acid, with the same phenomena. When heated, its behaviour is exactly similar to that of phosphorous acid.

* Hypophosphorous acid forms with all the bases salts which are soluble in water; wherefore the solutions of earthy and of metallic salts produce no precipitates in solutions of hypophosphites, unless the metallic oxyde be thereby reducible; but this reduction is much more easily effected than with phosphorous acid and its salts. Gold is promptly precipitated in the metallic state from its solutions. The neutral solutions of silver produce in the solution of a hypophosphite a precipitate which at first is white, but which very rapidly turns brown, and which, after a time, even in the cold, consists of black metallic silver: this phenomenon is accelerated by heat. A solution of protochloride of mercury, to which muriatic acid has been added, gives a precipitate of metallic mercury, when a large quantity of solution of hypophosphorous acid, or of a hypophosphite, is added; in the contrary case, that is, if the solution of protochloride of mercury (sublimate) is in excess, subchloride of mercury (calomel) only is produced, but much more abundantly than with an equal quantity of phosphorous acid, or of phosphite. This, therefore, is a good way of distinguishing the presence of hypophosphorous acid and of hypophosphites. Protosalts of copper are reduced only when the liquids are very concentrated, and heated for a long time.

* In the solid state, all the hypophosphites are decomposed by a red heat. When calcined in a small retort, as mentioned above (page 274) respecting the phosphites, if the neck of the retort be plunged under water, most of these salts disengage phosphuretted hydrogen, which for the most part inflames spontaneously on coming in contact with the air, and burns with emission of white fumes, leaving at the surface of the water a yellowish-brown deposit of phosphorus. If this gas be made to pass through a solution of nitrate of silver, the least bubble is sufficient to determine a blackish-brown colouring: and a larger quantity of gas produces a black precipitate, which becomes white by standing, or by the action of heat, and which consists of pure silver; the liquor then contains phosphoric acid; if through a

solution of perchloride of gold, the precipitate consists of metallic gold. If the gas be passed through a solution of protochloride of mercury (sublimate), a yellow precipitate is produced. When the hypophosphites are decomposed by a red heat, a feeble trace of phosphorus is sublimed, and there remains a neutral phosphate, which appears a little reddish or brownish after cooling, but which has no colour whilst heated.

The neutral phosphate thus produced is easily dissolved by muriatic acid, leaving a very small portion of an insoluble red substance, which contains phosphorus. The combinations of hypophosphorous acid with the fixed alkalies, the earths, and most metallic oxydes, are thus decomposed by a red heat. The hypophosphites of nickel and of cobalt are the only compounds which, when ignited, disengage during decomposition a mixture of hydrogen gas and of phosphuretted hydrogen gas, which does not spontaneously ignite on coming in contact with the air, and there remains an acid metallic phosphate, which is insoluble in muriatic acid, because it has been ignited, and which becomes soluble in water only after being boiled in concentrated sulphuric acid.

* When hypophosphorous acid, or a hypophosphite, is boiled with an excess of a concentrated solution of POTASH or of SODA, there is an abundant disengagement of pure hydrogen gas, and the hypophosphorous acid is entirely converted into phosphoric acid. In the same manner, when baryta, strontia, or lime is added to the solution of a hypophosphite, hydrogen is disengaged, and the hypophosphite is converted into a phosphate; but this conversion is less rapid than when potash or soda is employed. This reaction may serve to distinguish hypophosphites from phosphites. (Page 275.)

* Free hypophosphorous acid cannot be confounded with any other acid except phosphorous acid. In order to distinguish these two acids from each other, they are to be cautiously saturated by means of a fixed alkali, or still better by an alkaline earth, for example, baryta, and the solution is to be evaporated to dryness, and the dry salt is then to be heated to redness in a

small retort, over a spirit lamp. If inflammable phosphuretted hydrogen gas is then evolved (*gas phosphure trihydrique*), either spontaneously inflammable, or which, being set fire to, emits white fumes, the acid was hypophosphorous acid; but if the phosphuretted hydrogen gas is not spontaneously inflammable, but, being set fire to, burns with a blue flame without emitting white fumes, the acid was phosphorous acid. When the analyst has a sufficient quantity of hypophosphorous acid, it may be recognized, because its solution, even if concentrated, being carefully saturated by an alkali, does not give any precipitate in solutions of salts of earths, or of metallic bases, which is not the case with phosphorous acid.

* The property which the hypophosphites possess, except those of cobalt and of nickel, of disengaging gaseous trihydroguret of phosphorus, when exposed to a red heat in a small retort, is so characteristic, that they cannot be confounded with other salts.

9. BORACIC ACID, BO_3.

(*Acide Borique.*)

Pure boracic acid is a colourless, transparent, and brittle glass, which fuses at a dark red heat, and does not volatilise[1]. After fusion in platinum vessels, boracic acid is somewhat difficultly soluble in water. If it be then dissolved in hot water, the liquid, on cooling, deposits crystalline scales, which have the shining appearance of mother-of-pearl, and feel unctuous to the touch. They consist of hydrate of boracic acid, sparingly soluble in water[2]. The solution reddens blue litmus paper, but it *renders turmeric paper brown, like an alkaline solution.* When an aqueous solution of boracic acid is slowly evaporated, a large portion of it volatilises with the aqueous vapour[3]. Boracic acid is soluble in alcohol, to the flame of which it imparts a green colour, which becomes more especially distinct when the solution is stirred, or towards the end, when the alcohol is nearly all consumed. This colouring imparted to the flame of alcohol, is the most distinctive character of boracic acid. When the alcoholic solution of this acid is evaporated, the vapours of the alcohol carry away a large quantity of the acid.

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[1] At the ordinary temperature, boracic acid is one of the weakest acids known; but at a red heat it displaces most of the acids which are more volatile than itself. —Ed.

[2] Hydrated boracic acid is soluble in 30 parts of cold and 3 of boiling water; the latter deposits pearly scales on cooling. The pure acid is not deposited from its aqueous solution in scales, but in small prisms.—Ed.

[3] This acid begins to volatilise with the aqueous vapour even before the water boils.—Ed.

Amongst borates, those only which have an alkaline base are very soluble in water[1]. * The neutral combinations of boracic acid with the earths and the metallic oxydes are insoluble, or at any rate, most of them are sparingly soluble, in water; wherefore the neutral solutions of the salts, the base of which is an earth or a metallic oxyde, produce precipitates in the neutral solutions of alkaline borates only when they are not too dilute. Such is the case, for example, when the solutions of borates are mixed with a solution of CHLORIDE OF BARIUM, which, however, must not be too dilute. The precipitate which results from this reaction is completely soluble in a large quantity of water; it is more soluble still in a solution of sal ammoniac, or in an excess of chloride of barium. The precipitate which a solution of CHLORIDE OF CALCIUM determines in those of borates is more soluble still than borate of baryta in water, and especially in a solution of sal ammoniac or of chloride of calcium. The precipitates which a solution of NITRATE OF LEAD produces in those of borates are much less soluble.

* A solution of NITRATE OF SILVER produces in concentrated solutions of borates a white precipitate of borate of silver, which is completely soluble in a large quantity of water, without undergoing decomposition. A very dilute solution of a borate causes in that of nitrate of silver a brown precipitate, insoluble in any quantity of water, and which consists of oxyde of silver without boracic acid. The two precipitates, that of borate of silver and of pure oxyde of silver, are very soluble in dilute nitric acid and in ammonia.

* A solution of PROTOCHLORIDE OF MERCURY determines in

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[1] These solutions of borates of alkalies react upon turmeric paper like a free alkali.—ED.

solutions of borates a brownish-red precipitate, which is a compound of protoxyde of mercury and protochloride of mercury, and which contains no boracic acid: the precipitate is insoluble in water.

* A solution of SUBNITRATE OF MERCURY produces a brown precipitate in those of borates.

When soluble borates are decomposed by boiling them with dilute SULPHURIC ACID, crystalline spangles of boracic acid, which are sparingly soluble, are formed as the liquor cools. These spangles may be recognized by the characters which have been related above; but it is necessary to wash them before with a little water, in order to expel the sulphuric acid which might adhere as well as the sulphate formed.

When, after having pulverised the borates, they are moistened with a few drops of (concentrated) sulphuric acid in a small capsule of porcelain, or in a crucible of platinum, and, alcohol being poured upon the mass, it is inflamed, it burns with a green flame, the hue of which becomes more distinct by stirring the liquor[1]. It is worthy of remark that metallic chlorides upon which sulphuric acid and alcohol are poured may communicate to the flame of the latter a greenish-blue colour, which is due to the muriatic ether produced during the reaction, but which does not resemble much that which is determined by boracic acid.

* When the borates which contain water of crystallisation are heated, they often produce an extraordinary intumescence whilst parting with their water. After having lost their water, and by continuing the heat, they fuse tranquilly into a liquid, which forms a glass on cooling[2].

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[1] According to Dr. Fresenius, this test may be rendered much more delicate by heating the vessel which contains the alcoholic mixture, and the alcohol being inflamed, to allow it to burn for some little time, extinguishing it, and again inflaming it, when the border of the flame will appear green, even though the quantity of boracic acid be so minute that it would fail to produce the characteristic reactions by treatment in the usual way.—ED.

[2] The borates which have been mixed with sulphuric acid, or retain as yet a small quantity of that acid, should never be exposed to a red heat in platinum crucibles; for although boracic acid and sulphuric acid have separately no action upon platinum, yet their combination attacks them powerfully. It likewise corrodes porcelain crucibles.—ED.

According to Turner, the borates can be detected before the blow-pipe by mixing them with a mixture of one part of pulverised fluor-spar, and four and a half parts of bisulphate of potash; the whole is to be moistened with a little water, and exposed on a wire of platinum to the point of the interior flame; a short time after the fusion, a green colour is observed round the flame, which soon vanishes, not to re-appear again.

The best character for detecting boracic acid is the green colour which this acid in a free state, as well as the borates decomposed by sulphuric acid, communicate to the flame of alcohol.

10. SILICIC ACID, SiO_3.

(Acide Silicique.)

PURE silicic acid, artificially prepared, is a white powder which grits between the teeth. It is found in nature in a crystallised state in rock crystal, and in a compact state in quartz; it is then white or else coloured by very minute traces of deutoxyde of manganese, of peroxyde of iron, or of organic matter, as, for example, in cornelian[1]. Glass is slightly scratched by rock crystal and by quartz; but these two substances are not so hard as diamond and some other gems[2].

As found in nature, silicic acid is insoluble in water, and in almost all acids. After exposure to a red heat, artificial silicic acid is perfectly insoluble in water, and in most acids. Its insolubility in water renders it incapable to expel the carbonic acid from the solutions of carbonates, and consequently it may be mixed with their solutions without causing an effervescence; but when silicic acid is fused with the alkaline carbonates, it combines with these bases, and carbonic acid escapes with effervescence. When silicic acid is thrown into carbonate of potash or of soda in a state of fusion, the fused mass effervesces in the same manner as when the solution of an acid is poured into that of a carbonate[1].

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[1] According to Gaultrier de Claubry, the colour of the red cornelian is owing to a carbonaceous matter, which, like other organic products, can be destroyed by calcination.—ED.

[2] Silicic acid is the most abundant solid mineral in nature. In order to obtain it perfectly pure, the precipitate formed by hydrofluosilicic acid gas in water, is to be washed two or three times, drying and gently igniting it in order to expel all traces of hydrofluoric acid. In this state it is a white powder, in an excessive state of division, and so light that a breath of air is sufficient to waft it away.—ED.

HYDROFLUORIC ACID is the only acid which easily dissolves the powder of ignited or of natural silicic acid. The more concentrated the solution of hydrofluoric acid is, the more easily does silicic acid dissolve in it. When the hydrofluoric acid is concentrated enough to emit fumes in the air, so much heat is evolved whilst the silicic acid is dissolving that the whole mixture becomes boiling. This experiment must necessarily be made in metallic vessels, because the silicic acid contained in glass is likewise attacked by hydrofluoric acid.

The silicic acid prepared by artificial means, and separated from its compounds, is a modification of that which occurs in the state of nature, as rock crystal and quartz, for it is not completely insoluble in water and in acids; far from it, since, on the contrary, it sometimes can be thus dissolved with the greatest facility. When separated from chloride of silicium, but more especially still from fluoride of silicium, by means of water, a small quantity remains dissolved in that menstruum, which, however, does not thereby acquire any taste, nor the property of reddening litmus paper. The silicic acid cannot be recognized in this solution except by evaporating the liquor almost to dryness; and by pouring water upon the residuum, silicic acid is separated in an insoluble state.

A solution of POTASH with the help of heat easily dissolves the silicic acid which has been dried, but not ignited, and the solution does not become gelatinous on cooling.

Solutions of CARBONATE OF SODA, or of CARBONATE OF POTASH, dissolve likewise with ease, and with the help of heat the silicic acid which has been dried; but the liquor on cooling stiffens into an opalescent jelly, which is so much the more stiff and rapidly formed, as the solution is more concentrated.

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[1] Pure silicic acid may be fused per se. M. Gaudin succeeded in effecting this by submitting it to the intense heat of the oxyhydrogen blow-pipe. When fused, it remains viscid like glass, and at a temperature a little above the fusing point it sublimes under the form of a thin vapour, which may be condensed. This sublimate is due probably to the aqueous vapour resulting from the combination of the detonating mixture used to fuse it, and by which it is carried away, as is the case, for example, with boracic acid (see note, page 279), which, not being volatile per se, yet flies off with the aqueous vapour of its boiling solution.—ED.

* Silicic acid which has been ignited, and that found in nature as rock crystal and quartz, are also soluble, the latter after being reduced into fine powder, in the solutions of pure alkalies, and of the fixed alkaline carbonates; but they are dissolved with much more difficulty than that which is artificially prepared and not ignited.

* The combinations of silicic acid with the fixed alkalies are always soluble in water, even when they contain a considerable excess of silicic acid. It is true that they are almost insoluble in cold water, but when in powder, boiling water dissolves them. The combinations of silicic acid with the other bases are insoluble; the double salts composed of silicates of alkalies and of silicates of earths, or of metals, which constitute ordinary glass, are likewise insoluble.

The alkaline silicates which contain a great excess of base are soluble in water. The more considerable the quantity of the silicic acid contained in these combinations, the more difficult they are to dissolve in cold water; and when they contain a very large proportion of silicic acid, they altogether resist the action of water and of acids, hydrofluoric acid only being excepted. Glass is amongst the number of such combinations.

* The presence of the alkali in glass is difficult to ascertain in qualitative analysis. To effect this, it is necessary to reduce the persilicate of alkali in fine powder, to put it in a platinum crucible, to pour upon it some concentrated hydrofluoric acid, to add sulphuric acid, and evaporate the whole to dryness; the alkali remains in the state of sulphate, and may thus be easily recognized.

When the silicates of alkalies containing a great excess of base are dissolved in water, and the solution is supersaturated with muriatic acid, the modification of silicic acid, which is easily soluble, is set free, and remains completely dissolved, provided the liquor be sufficiently diluted with water, and no precipitate is formed. But if the same basic alkaline silicate has been dissolved only in a small quantity of water, and the solution be saturated with an acid, the greatest part of the silicic acid is separated under the form of a jelly, or of gelatinous flakes, which the addition of a larger quantity of water does not dissolve, though another portion of the silicic acid remains dissolved in the acid liquor. Consequently, the more the aqueous solution of the basic alkaline silicate is diluted, the less abundant the quantity of silicic acid separated by supersaturating it with acids is; nay, if this solution is very dilute, it often occurs that no silicic acid is separated, as we have said above. On the contrary, the more concentrated the solution is, the larger also is the quantity of silicic acid separated by supersaturating it with acids; and at a certain degree of concentration the silicic acid thus separated is so abundant that the whole liquor stiffens into a thick mass.

If the supersaturated liquid from which a small quantity of silicic acid, or none, has separated, be evaporated, and after having attained a certain degree of concentration if it be left to cool, the silicic acid separates therefrom under the form of a transparent jelly, resembling much that which is produced when a solution of animal glue in boiling water is cooling. By pouring water upon this jelly the greatest part of the silicic acid is separated under the form of thin insoluble flakes, but there is a portion of the acid which dissolves in the water. If the evaporation of the jelly is carried to complete exsiccation, the whole of the silicic acid remains insoluble.

The basic combinations of silicic acid with baryta, strontia, and lime behave, at least towards acids, in a manner analogous to that of the basic alkaline silicates. When treated by muriatic acid, the greatest portion of the silicic acid is separated, but a portion of this acid remains dissolved, and forms a jelly when the acid liquor is concentrated by evaporation; and in this case, also, for the purpose of separating the silicic acid entirely, it is necessary to evaporate the jelly to dryness, and to treat the dried mass by water.

The combinations of silicic acid with non-alkaline bases are insoluble in water. With respect to their behaviour towards acids, they may be divided into two classes. In effect, some of them are decomposed by the strong acids, such as concentrated muriatic acid; the others resist the action of the most powerful acids.

The silicates which are decomposable by muriatic acid are not all decomposed in the same manner. When, after reducing the salt into fine powder, muriatic acid is poured upon it in the cold, it is often decomposed all of a sudden, much heat is evolved, and the whole stiffens into a gelatinous magma. If water be then poured upon this mass, the bases which before were combined with the silicic acid are dissolved in the state of metallic chlorides, and the silicic acid remains under the form of delicate flakes. To this class the silicates which are found in nature under the name of zeolites belong, and especially those amongst them which contain water of crystallisation; yet in most cases they are scarcely attacked by muriatic acid when they have been ignited. But it often occurs that the pulverised silicates are attacked by muriatic acid only after a prolonged digestion therein, and without production of a jelly or of a gelatinous mass: in these instances, the silicic acid is separated under the form of a fine powder.

The silicates which resist the action of acids are decomposed, with disengagement of carbonic acid, when their powder is ignited with three times its weight of carbonate of potash or of soda. The pulverised silicate is mixed with the alkaline carbonate also in powder in a platinum crucible, and the mixture is to be ignited. If the combination contains much silicic acid, a fused mass is obtained after ignition; if the silicic acid is in less quantity, the mass after ignition is only agglomerated: in either case, the mass being treated by dilute muriatic acid, the bases which were combined with the silicic acid are dissolved in and unite with the muriatic acid, and the greatest part of the silicic acid is separated; but a certain quantity of it remains in solution, which forms a jelly, when the liquor is brought by evaporation to a certain degree of concentration. If, however, there is but little silicic acid in the combination, it often may occur that the calcined mass dissolves entirely in the dilute muriatic acid.

Many silicates seem at first to resist altogether the action of acids; yet by prolonged digestion in the acid they ultimately are decomposed, especially when sulphuric acid diluted with a small quantity of water is employed. By a prolonged digestion in sulphuric acid, nearly all silicates are decomposed.

A small number of silicates are not decomposed, either by acids or by fusion with alkaline carbonates. Their decomposition can be effected only by reducing them in extremely fine powder, mixing them with three times their weight of pure potash, and igniting them in a silver crucible.

The following silicates, which are found in nature, are completely decomposed by muriatic acid.

	COMBINATION OF
1. Apophyllite	[Potash, silica, lime, and water.]
2. Natrolite	[Silica, soda, and water.]
3. Scolezite	[Silica, alumina, lime, soda, and water.]
4. Mesolite[1]	Do. do. do.
5. Mesole	Do. do. do.
6. Analcime	[Silica, alumina, soda, water.]
7. Laumonite	[Silica, alumina, lime, and water.]
8. Potash harmotome	[Silica, alumina, baryta, potash, and water; sometimes lime.]
9. Leucite	[Potash, silica, and alumina.]
10. Eleolite	[Silica, alumina, lime, potash, soda, and water.]
* 11. Brewsterite	[Silica, alumina, strontia, baryta, lime, and water.]
12. Sodalite	[Soda, silica, and alumina, with a small quantity of muriatic acid.]
13. Cronstedtite	[Silica, oxyde of iron, water.]
* 14. Ilvaite	[Silica, protoxyde of iron, and lime.]
15. Gehlenite	[Silica, alumina, lime, oxyde of iron.]
16. Wernerite	[Silica, alumina, lime, soda.]
17. Tabular spar	[Silica and lime.]
18. Nepheline	[Soda, silica, and alumina.]

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[1] Scolezite and mesolite have nearly the same crystalline form, and the same physical and chemical characters.—Ed.

	COMBINATION OF
* 19. Cancrinite[1] .	. [Soda, silica, and lime.]
* 20. Mellinite .	. [Silica, magnesia, lime, oxyde of iron.]
21. Chabasite .	. [Silica, alumina, lime, water with a little silica and potash.]
22. Pectolite .	. [Silica, lime, soda, potash, water, oxyde of iron.]
23. Okenite .	. [Silica, lime, soda, and potash, oxyde of iron, oxyde of manganese, water.]
24. Davyne . .	. [Silica, alumina, lime, iron, water.]
25. Gadolenite .	. [Yttria, silica, glucina, oxydes of cerium and iron.]
26. Allophane .	. [Alumina, silica, water.]
27. Helvine .	. [Silica, glucina, alumina, and protoxyde of iron and of manganese.]
28. Datholite .	. [Silica, boracic acid, lime, water.]
29. Botryolite .	. [Differs from precedent in containing 1 atom more of water.]
30. Haüyne . .	. [Potash or soda, silica, alumina, lime, and sulphuric acid.]
31. Nosian .	. [Sesquisilicate of alumina and soda (Klaproth).]
32. Lazulite .	. [Silica, alumina, lime, oxyde of iron, magnesia, soda, and sulphuric acid.]
33. Eudialite[2]	. [Silica, soda, zirconia, lime, oxydes of iron and manganese, muriatic acid and water.]
34. Orthite . .	. [Silica, alumina, oxydes of iron, cerium, lanthanum, manganese, lime, yttria, magnesia, and small quantity of water.]
35. Electric calamine[3]	[Oxyde of zinc, silica, and water.]
* 36. Sidéroschisolite	. [Protoxyde of iron, silica, alumina, and water[4].]
* 37. Hisingerite	. [Silicate of protoxyde and sesquioxyde of iron + 6 atoms of water.]

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[1] This mineral, discovered by Hoffman, is thought by some mineralogists to be the same as sodalite. Their respective analysis is as follows :—

	SODALITE.				CANCRINITE.
	FROM GREENLAND.		FROM VESUVIUS.		MINES IN SIBERIA.
	Eckeberg.	Thomson.	Arfwedson.	Watchmeister and Berzelius.	Hoffman.
Soda . .	25·00	25·50	26·55	20·96	24·47
Silica . . .	36·00	38·52	35·99	50·98	38·40
Alumina . .	32·00	27·48	32·59	27·64	32·04
Lime . . .	0·00	2·70	0·00	0·00	0·32
Muriatic acid .	6·75	3·06	5·30	1·29	
Protoxyde of iron	0·25	1·00	0·00	0·00	
Volatile matter .	0·00	2·10	0·00	0·00	loss 4·77
	100·00	100·00	100·00	100·00	100·00

[2] According to M. Beudan, sulphate of zirconia, and silicate of soda, lime, and iron.—Ed.

[3] This mineral must not be confounded with calamine, which is a carbonate of zinc, whilst the other is a silicious oxyde of zinc, or rather a hydrated silicate of zinc.—Ed.

[4] This mineral is probably a basic silicate of iron, and the alumina an accidental ingredient.—Ed.

	COMBINATION OF
38. Dioptase	[Silicate of copper and water.]
39. Meerschaum	[Magnesia, carbonic acid, silica, water, a little alumina, and traces of manganese and lime.]
40. Copper malachite	[Carbonate and silicate of copper and water.]
41. Stilbite[1]	[Silicate of alumina, of lime, and water.]
42. Epistilbite[2]	[Silicate of alumina, of lime, and water.]
43. Heulandite	[Tersilicate of alumina and of lime.]
44. Anorthite	[Silica, alumina, lime, magnesia.]
45. Sphene or Titanite	[Tersilicate of lime, and titaniate of lime.]
46. Pyrosmalite	[Lime, tersilicate of oxyde of iron and of manganese.]
47. Cerite	[Hydrated silicate of peroxyde of cerium.]
48. Cerine or Allanite	[Silicate of alumina and of cerium, of iron and of lime.]
49. Pitchblende[3]	[Uranium ore.—Ed.]

The first forty of these compounds when pulverised form a jelly when muriatic acid is poured upon them, which is not the case with the remainder, some of which are completely decomposed only by reducing them to an extremely fine powder and digesting them for a long time in hot muriatic acid. Most of these compounds, though not all, after ignition, resist the action of acids. Some of them especially, among the last named, are decomposed by acids, even after they have been ignited.

The following silicates, which are found in nature, absolutely withstand the action of acids even after fine pulverisation; therefore, other means must be resorted to for the purpose of analysing them, which is accomplished by fusing them with carbonate of potash, or of soda; they are—

1. Felspar
2. Albite
3. Rhiacolite
4. Petalite
5. Spodumene (*Soda spodumene*)
6. Oligoclase
7. Labradorite
8. Barytic harmotome
9. Olivine
10. Prehnite
11. Carbonated manganese
12. Mica

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[1] The formula of epistilbite, according to Beudan, $3\ Al_2O_3Si + CaO,\ SiO_3 + 5$ aq., that of stilbite $3\ Al_2O_3 + CaO,\ SiO_3 + 6$ aq. The difference consists therefore in 1 atom of water.—Ed.

[2] The formula is $4\ Al_2O_3,\ 3\ SiO_3 + CaO,\ 3\ SiO_3 + 6$ aq. That is to say, 4 atoms of tersilicate of alumina, and 1 atom of tersilicate of lime, and 6 atoms of water, being the mean of two analyses by Walmsted and Thomson.—Ed.

[3] This ore contains from 2 to 5 per cent. of silica, probably in a state of mechanical, not of chemical combination.—Ed.

13. Lepidolite
14. Talc
15. Chlorite
16. Pinite
17. Achmite
18. Amphibole
19. Anthophyllite
20. Pyroxene
21. Diallage
22. Chatoyant spar [1]
23. Epidote
24. Idocrase
25. Garnet
26. Dichroite
27. Emerald
28. Euclase
29. Phenakite
30. Tourmaline
31. Axinite
32. Topaz
33. Chondrodite
34. Picrosmine
35. Carpholite
36. Steatite
37. Serpentine
38. Pumice stone
39. Obsidian
40. Pitchstone.

To this class belong also the different species of artificial glass and the false gems.

Amongst the silicious compounds which resist both the action of acids and fusion with carbonate of potash or of soda, but which are completely decomposed by ignition with pure potash, the following are the only ones found native, namely:—

1. Zircon
2. Cyanite
3. Cymophane
4. Staurolite
5. Andalusite

Before the blow-pipe silicic acid may be recognised, because it is almost insoluble; or it dissolves only in extremely small quantity in microcosmic salt, even after protracted blowing. Whilst being thus treated the silicic acid floats in the fused bead and forms a swollen, translucid mass, which is better perceived during fusion than after cooling. When a silicate is treated with microcosmic salt before the blow-pipe, the bases dissolve in this flux, and the silicic acid thus liberated swims in the bead. Silicic acid, on the contrary, dissolves completely in borax, but the solution is very slow. Treated by soda before the blow-pipe, upon charcoal, it fuses into a perfectly limpid glass, and carbonic acid is disengaged with effervescence.

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[1] Also called Schiller spar.—Ed.

There are but few substances which, treated with soda before the blow-pipe, produce a bead in fusing, and amongst them silicic acid is the only substance which thus forms a colourless, limpid, and transparent glass, by which characters it may therefore be easily recognised. Even when the silicic acid contains a small portion of an earth, it still forms a clear bead by fusion with soda. Such is particularly the case with felspar. But the more earths a silicate contains, or in general when it contains no alkali, the more infusible the combination is with soda, especially when much soda is used.

Silicic acid differs from other substances, because after ignition it is insoluble in all acids except in hydrofluoric acid. The character most to be depended on to detect its compounds, and distinguishing them from all other substances, is its behaviour towards microcosmic salt and soda [1].

11. TANTALIC ACID, TaO_2.

(Acide Tantalique.)

* In the pure state tantalic acid forms a white infusible powder, which does not redden moistened litmus paper. It is quite insoluble in acids and in solutions of alkalies, but it dissolves in caustic potash by fusion; treated in the same manner with the fixed alkaline carbonates, it combines with their base, and carbonic acid is disengaged with effervescence. It is also dissolved by fusion with bisulphate of potash. When the mass resulting from the fusion of tantalic acid with bisulphate of potash is treated by water, the acid remains undissolved in the state of a hydrate.

* Hydrated tantalic acid is a powder of a milky white colour, insoluble in water, but which being spread upon litmus paper in a moist state reddens it [2]. It is very sparingly soluble in

concentrated SULPHURIC ACID; but water reprecipitates it from such a solution[1]. HYDROFLUOSILICIC ACID dissolves it completely; but in all other acids it is either wholly insoluble, or very sparingly soluble. It is pretty largely dissolved by boiling it in a solution of BINOXALATE OF POTASH; the liquid obtained is colourless, but the alkalies reprecipitate the tantalic acid from such a solution[2], in which FERROCYANURET OF POTASSIUM produces a yellow, and INFUSION OF GALLS an orange-yellow precipitate. Even when infusion of galls is poured upon hydrated tantalic acid, it assumes an orange-yellow colour, and the supernatant liquid becomes yellow.

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[1] Care should be taken not to use too large a proportion of soda, else the bead will not be clear or colourless. The bead produced is of course silicate of soda, and during the fusion there is a disengagement of carbonic acid from the decomposition of the carbonate of soda employed.—Ed.

[2] When hydrated tantalic acid is heated in a retort, it abandons pure water which is not in any way acid, and is converted into anhydrous tantalic acid, but it at the

* Hydrated tantalic acid is soluble in SOLUTION OF POTASH, wherefore when ignited tantalic acid is fused in a silver crucible with caustic potash, the fused mass may be dissolved by water. From such a solution tantalic acid may be precipitated by muriatic acid and other acids, in an excess of which it is insoluble. But when it is fused with alkaline carbonates, the resulting tantalate of potash does not dissolve in water, because tantalate of potash is insoluble in excess of alkaline carbonate; when, however, the excess of alkaline carbonate has been removed by cold water, the tantalate of potash may be dissolved by boiling water. The carbonic acid of the air is even sufficient to precipitate the tantalic acid from such a solution.

* HYDROSULPHURET OF AMMONIA has no action upon hydrated tantalic acid. When this re-agent is added to a solution of tantalic acid in binoxalate of potash, the acid is precipitated by the ammonia, and sulphuretted hydrogen gas is disengaged.

* Before the BLOW-PIPE, tantalic acid is dissolved by microcosmic salt into a limpid glass, a character which distinguishes it from silicic acid. It dissolves in borax, producing a limpid

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same time loses the power of reddening litmus paper. The hydrate contains, according to Berzelius, 11½ per cent. of water.

[1] The precipitate thus reproduced by water retains a certain portion of sulphuric acid with energy.—ED.

[2] If the tantalic acid contains any tungstic acid, the saturated solution stiffens on cooling into a milky jelly, and if a small piece of zinc or of tin be introduced therein it becomes bluish.—ED.

colourless glass, but which becomes milky either the instant it cools, or when, after it has cooled, it is again gently heated. This character also distinguishes it from silicic acid. Tantalic acid combines with soda with effervescence; but it is not reduced by it upon charcoal.

* Tantalic acid differs from a great number of substances, because after ignition it is insoluble in all solvents; but that which distinguishes it best from all other substances is its solubility in water after fusion with pure potash, in which alkaline solution muriatic acid produces a milky white precipitate of oxyde of tantalum, insoluble in an excess of muriatic acid. It differs also from silicic acid by its behaviour before the blow-pipe.

12. TITANIC ACID, TiO_2.

(*Acide Titanique.*)

* Pure titanic acid forms a white powder, when it has been prepared by igniting the hydrated titanic acid which has been precipitated by boiling from its solution in muriatic acid. But when it has been precipitated from its solution by means of an alkali, and then ignited, it forms a cohesive clotty precipitate of a very light-brownish tinge, which has much lustre. Titanic acid has sometimes a reddish colour, which, however, is owing to the presence of a feeble trace of peroxyde of iron. When heated, it assumes a lemon-yellow hue, which vanishes on cooling, and then it becomes white again.

* Ignited titanic acid is insoluble in all acids, except in boiling concentrated sulphuric acid, which dissolves it with the help of heat. When ignited with the fixed alkalies, either pure or carbonated, it combines with them, and when the ignition is performed with the carbonates, the carbonic acid is disengaged with effervescence. The fused compound is crystalline, and by treating it with water, the excess of alkali is taken up, and an acid titaniate of alkali is left, which is soluble in muriatic acid when digested with the help of a very gentle heat. But if this acid solution be boiled for a long time after having diluted

it with water, the greatest part of the titanic acid separates under the form of a heavy white precipitate[1]. When this precipitate is gathered on a filter, the liquor passes clear through the paper, so long as it continues to be acid; but if the titanic acid be washed with pure water, the liquid traverses the thickest paper with a milky colour, and mechanically carries away all the acid, until by protracted washing, none of it ultimately remains on the filter. The titanic acid, which is precipitated by ebullition from solutions of titaniates of alkalies in muriatic acid, is only slightly soluble in acids; if, on the contrary, it has been precipitated by ammonia, it may be easily filtered, and is completely soluble in acids, even after washing it with cold water; when, however, it has been washed with hot water, it is not completely soluble in acids[2].

* White bulky precipitates of hydrated titanic acid are produced in muriatic acid solutions of titaniates of alkalies by solutions of POTASH, of AMMONIA, of CARBONATE OF POTASH, of BICARBONATE OF POTASH, and of CARBONATE OF AMMONIA. These precipitates are not soluble in an excess of the re-agent[3]; but the titanic acid of which these precipitates consist is completely redissolved by an excess of muriatic and of several other acids; a solution of sulphurous acid does not wholly dissolve it,

unless care has been taken to avoid heat, as much as possible, during the precipitation, and to use hot water for washing it. The alkaline carbonates dissolve small quantities of titanic acid, but the proportion is so trifling as not to be taken into account in qualitative analysis.

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[1] The precipitation of the titanic acid is more completely effected by dissolving the titaniate of alkali in concentrated sulphuric acid, instead of muriatic acid, and then diluting the solution with a large quantity of water.—ED.

[2] Berzelius remarks, that ignited titanic acid may be again rendered soluble by any of the following treatments:—1st, By fusing with carbonate of potash. 2nd, By reducing it into very fine powder, and digesting it in concentrated sulphuric acid, with the help of a temperature sufficient gradually to evaporate the excess of acid. 3rdly, By mixing it with pulverised charcoal, and exposing the mixture to a red heat in a current of chlorine gas, by which means a liquid chloride of titanium is obtained, which may be subsequently diluted with water.—ED.

[3] Berzelius says, that titanic acid recently precipitated by ammonia from its solutions in acids, is dissolved in small quantity by the alkaline carbonates without disengagement of carbonic acid. The experiments of our Author in 1846 also have proved that caustic ammonia entirely precipitates titanic acid from its solutions in either muriatic or sulphuric acids, which acids may be easily removed by washing; but the well washed precipitate obtained is an acid ammoniacal salt, composed of 87·69 per cent. of titanic acid, and 2·47 per cent. of ammonia, and 9·84 per cent. of water. $NH_3, TiO_2 + 4\ HO, TiO_2$.—ED.

* When the solution of the titaniates of alkalies in muriatic acid does not contain too much free acid—when, for example, it has been prepared in such a way, that part of the titaniates treated by muriatic acid has remained undissolved, and has been filtered from the solution diluted with water, white precipitates are produced by adding thereto dilute SULPHURIC, ARSENIC, PHOSPHORIC, TARTARIC ACIDS, but more especially OXALIC ACID. These precipitates consist of combinations of titanic acid with the acid employed; all are completely redissolved by an excess of the acid employed, and likewise by muriatic acid; yet the precipitate of oxalate of titanic acid requires a very large quantity of the acid to be redissolved. Other acids, such as *nitric, acetic, succinic* acids produce no precipitates in the solutions of the titaniates of alkalies in muriatic acid.

* When a solution of titaniate of alkali in muriatic acid contains the least possible quantity of this acid, INFUSION OF GALLS produces therein a reddish orange-yellow precipitate of tannate of titanic acid. If infusion of galls be poured upon titanic acid, which has been precipitated from its solution by boiling, it assumes a reddish orange-yellow, or a yellowish-brown colour.

* A solution of FERROCYANURET OF POTASSIUM produces a dirty deep-green precipitate of ferrocyanuret of titanium in acid solutions of titanic acid.

* SULPHURETTED HYDROGEN in aqueous solution, or in the gaseous state, produces no precipitate in the acid solutions of the titaniates of alkalies.

* When an excess of HYDROSULPHURET OF AMMONIA is poured in the acid solutions of titaniates of alkalies, a white precipitate of titanic acid is formed, and sulphuretted hydrogen is disengaged.

If, however, the solution contains traces, even very minute, of peroxyde of iron, the precipitate has a grey or a black colour.

* If a bar of METALLIC ZINC be plunged in a muriatic acid solution of a titaniate of alkali, the liquor assumes a blue colour, and at first remains limpid, whilst the free acid disengages hydrogen; but after a time a blue precipitate is formed, which gradually becomes white. If the zinc be removed, whilst the blue liquor is still clear, and an excess of solution of potash or of ammonia be poured therein, a blue precipitate is formed, which gradually becomes white, whilst hydrogen is disengaged. When titanic acid has been precipitated from its solution by boiling, and a piece of zinc is thrust in the precipitate, it assumes a blue colour, which begins from the zinc. When a solution contains only a small quantity of titanic acid, it is not rendered blue by zinc. Metallic iron and tin behave like zinc in this respect.

* All the combinations of titanic acid with the bases appear, as far as is known, to be soluble in concentrated muriatic acid, even after ignition, provided they have been brought to a state of fine division by levigation. The solution is expedited by the application of heat, which, however, must be very gentle, otherwise the dissolved titanic acid might be precipitated, and muriatic acid would not then re-dissolve it.

* In the course of chemical analysis the operator is often liable to overlook the presence of titanic acid in many titaniates, and sometimes, also, that of the bases with which it is combined. The presence of the bases may be detected in the combinations of titanic acid with the alkalies and alkaline earths by looking for them in the clear liquor filtered from the precipitate of titanic acid produced, by adding ammonia to the muriatic acid solution of these compounds. But when titanic acid is combined with bases which the alkalies can likewise precipitate from the muriatic acid solution, it is often difficult to separate the titanic acid from these bases in such a way as to be able to identify it. When these bases are susceptible of being precipitated

as metallic sulphurets, by means of sulphuretted hydrogen added to this acid solution, this re-agent may be employed to separate the titanic acid, the presence of which may subsequently be detected in the filtered liquid. If, on the contrary, the bases are precipitable as metallic sulphurets only in neutral or in alkaline solutions, and by means of hydrosulphuret of ammonia, (which is the case, for example, with protoxyde and peroxyde of iron, combined with which titanic acid is very frequently met in nature), it is often practicable in qualitative analysis to resort to boiling, in order to precipitate from its muriatic acid solution the titanic acid, which may then be submitted to subsequent examination; but when the compounds contain only very small quantities of titanic acid, as the acid cannot then be precipitated by boiling, the operator is obliged, after having dissolved the compound in muriatic acid, to add to the liquid a solution of a non-volatile organic substance, by which titanic acid, like most bases, as the reader may recollect, loses the property of being precipitated by alkalies. The solution which is best adapted to such a case is a solution of tartaric acid. After having poured this acid in the liquor, the solution is to be supersaturated with ammonia, which then causes no precipitate; after which hydrosulphuret of ammonia is to be added to this ammoniacal solution, in order to precipitate the metallic oxyde in the state of metallic sulphuret. The presence of the titanic acid in the liquor filtered from the precipitate, cannot be recognised unless by evaporating the solution to dryness, igniting the residuum in contact with the air until the ammonical salts be expelled, and also all the carbon of the tartaric acid burnt, after which, what is left is titanic acid. It is best, when the quantity of dry residuum obtained is large, to ignite it in a small platinum capsula placed in the muffle of a small assay furnace. When the quantity is less considerable a platinum crucible is sufficient.

* But when the base with which the titanic acid is combined is not susceptible of being converted by hydrosulphuret of ammonia into an insoluble metallic sulphuret, the greatest difficulty is often experienced, even in the course of purely qualitative

analysis, to separate titanic acid from its combinations, especially as its union with some bases at times communicates to it certain properties which in other circumstances it does not possess. This is more particularly the case with the native compound of titanic acid and zirconia. When, after having dissolved this combination in sulphuric acid, and diluted the solution with water, it is heated to ebullition, little or no titanic acid is precipitated, though ebullition completely precipitates titanic acid from its diluted solution in sulphuric acid when it exists alone; neither does a solution of *ferrocyanuret of potassium* produce any precipitate in the solution of these two substances. Even the zirconia cannot be precipitated free of titanic acid from such a solution by solution of sulphate of potash, for this re-agent precipitates also a solution of pure titanic acid; in order to obtain the pure zirconia it is necessary that the liquor should not contain too much free acid. The only available method to separate these two bodies in qualitative analysis, for the purpose of further examining each separately, is that of Berzelius; namely, by precipitating both substances from the solution by means of ammonia, igniting the precipitate, and fusing it in a platinum crucible with bisulphate of potash. The fused mass is then to be digested in water, and the combination of titanic acid and zirconia, which will have remained undissolved, is to be treated by concentrated muriatic acid, which only takes up the zirconia, which may be identified in the solution, whilst the titanic acid remains undissolved.

* When titanic acid is combined with other bases, which are soluble in a solution of potash,—for example, with alumina or glucina,—the separation may be attempted by this process; but if the bases are insoluble in the solution of potash, the separation of titanic acid must be tried by boiling.

* When both titanic acid and silicic acid are conjointly met with, combined with bases, the substance should be reduced to exceedingly fine powder, and digested with muriatic acid in a closed vessel. The titanic acid combined with the base dissolves, and the silicic acid remains undissolved. The digestion

must be effected in the cold or only at a very gentle heat, so as to avoid the separation of the titanic acid dissolved by the muriatic acid; for if the titanic acid has once separated it, it is impossible, as we have said, to re-dissolve it in any excess of muriatic acid. The silicic acid is separated by filtering, washed with cold water, and it may be recognised as such. As to the titanic acid which has dissolved, it may be separated from the bases.

* Before the BLOW-PIPE, titanic acid and its combination with the bases, which do not impart a colour to the fluxes, may be recognised; because, when dissolved in microcosmic salt, they communicate to the glass produced by exposing them for a long time to the action of the interior flame a blue or violet colour, which does not appear distinctly except after perfect cooling. Some titaniates require a prolonged treatment in the interior flame to impart this bluish tint to the bead after cooling. The addition of a little tin hastens the manifestation of the colour; but in all cases it disappears in the exterior flame. If the titanic acid contains iron, the bead heated in the interior flame becomes on cooling of a blood-red colour. Titanic acid treated with borax in the exterior flame produces a colourless glass, which becomes milky-white when heated again. Exposed in the interior flame this bead assumes a yellow tinge; but by a prolonged blowing it becomes purple, or even dark blue, after cooling; if the titanic acid be in large quantity, when this glass is heated again, it becomes of a light blue, and resembles an enamel. Several titaniates, such as sphene, for example, do not yield a blue glass by treatment with borax in the interior of the flame; but with microcosmic salt they do so. With soda, titanic acid fuses with effervescence upon charcoal, and produces a yellow glass, which becomes greyish-white and opaque on cooling.

* The properties of giving a blue or purple colour with microcosmic salt in the interior flame only, prevents titanic acid from being confounded with the oxyde of manganese, which assumes the blue or purple colour only in the exterior flame, and with oxyde of cobalt, which takes that hue both in the exterior and in the interior flame.

* Titanic acid is very well distinguished from other substances, because it is precipitated from its acid solutions by boiling, after which it is almost insoluble in muriatic acid; because zinc gives a blue colour both to its solutions and to its precipitate; but the most distinctive test is the blow-pipe.

* The presence of non-volatile **ORGANIC SUBSTANCES**, more especially of tartaric acid, completely prevents titanic acid from being precipitated by alkalies from its combinations in muriatic acid. Nor can it be precipitated by boiling from such solutions, whether they be acid or with excess of alkali. When to a solution of titanic acid in muriatic acid, tartaric acid is first added, then an excess of ammonia, infusion of galls produces in the liquor a precipitate, which instead of being orange-yellow, is of a dirty deep green, which requires a very long time for settling.

13. ACIDS OF ANTIMONY.

1°. ANTIMONIC ACID, SbO_5.

(Acide Antimonique.)

* **PURE** antimonic acid is yellow, but the hydrate is white. When heated to redness, it loses part of its oxygen, is converted into antimonious acid, and becomes white. Wherefore, when the hydrate is heated, it at first becomes yellow because it becomes anhydrous; but by a stronger heat it loses oxygen and becomes white. It is owing to this decomposition that when antimonic acid is exposed to a red heat, in a glass tube closed at one end, and the other extremity of which is drawn into a long point, if a glowing splinter be brought to the aperture, it is immediately kindled, and continues to burn vividly. Antimonic acid cannot be wholly converted into antimonious acid in a small glass retort; for after having been thus calcined, one may as yet perceive in the centre, portions which are yellow, and which disappear after ignition in a platinum crucible.

* Hydrated antimonic acid is insoluble in water, but it is soluble, though with difficulty, in concentrated muriatic acid, with the help of heat. The solution becomes turbid by addition

of water; if a large quantity of water be at once poured in, there is not at first much turbidness produced, but after some time, a white precipitate is formed, which is quite as abundant as if the water had been gradually added[1]. Antimonic acid and its hydrate are insoluble in nitric acid.

* When antimonic acid is fused with the fixed alkaline carbonates, carbonic acid is disengaged.

* Not only the hydrate, but even the anhydrous antimonic acid strongly reddens moistened litmus paper.

* Antimonic acid forms with all bases salts, which are either insoluble, or sparingly soluble. Its combinations, even with the alkalies, are not very soluble.

When a solution of CARBONATE OF POTASH is poured upon hydrated antimonic acid, the potash unites with the acid, but the resulting combination is not entirely soluble, even by the addition of much alkali and of much water. The same thing occurs when a solution of pure potash is used. Solutions of POTASH, of AMMONIA, of CARBONATE OF POTASH, and especially of BICARBONATE OF POTASH, produce also in muriatic acid solutions of antimonic acid white precipitates, a great portion of which, though not all, dissolves in an excess of the re-agent. The precipitate thus formed is best and completely re-dissolved by an excess of solution of pure potash. The solution of antimonic acid in potash may be diluted with water without becoming turbid. Dilute muriatic acid, and nearly all other acids, even a current of carbonic acid gas, precipitate antimonic acid therefrom in the state of a hydrate.

* When antimonic acid is fused with pure *potash* or *carbonate of potash*, and the fused mass is treated by water, part of the combination of the antimonic acid with the potash remains undissolved, whilst the other portion is taken up. This solution behaves with acids like a solution of hydrated antimonic acid in potash. According to Berzelius, the portion dissolved in the water is a basic antimoniate of potash, whilst the insoluble

portion is an acid antimoniate of potash. The compound which dilute acids precipitate from a potash solution of antimonic acid is likewise an acid antimoniate of potash. When antimony or sulphuret of antimony is deflagrated with an excess of nitrate of potash, and the residuum treated by water, the same combinations are formed.

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[1] It often occurs that the solution remains limpid. This character distinguishes it from antimonious acid, which is always rendered immediately turbid by such treatment.—ED.

* Most of the combinations of antimonic acid with the bases are decomposed by nitric acid, which dissolves the base and leaves the antimonic acid. But generally, when the antimoniates have been ignited, which operation is often accompanied with a disengagement of light[1], they can no longer be decomposed by acids.

* The most distinctive character of antimonic acid is, that SULPHURETTED HYDROGEN, either in aqueous solution or in the gaseous state, produces in its muriatic acid solution an orange-yellow precipitate, which has a hue sufficiently characteristic to distinguish it from that produced by the same re-agent in the acid solution of oxyde of antimony. HYDROSULPHURET OF AMMONIA easily dissolves this precipitate, which however re-appears by adding a dilute acid; but then it has a lighter colour than before, and often it appears quite yellow, when a large quantity of sulphur, arising from the decomposition of the hydrosulphuret of ammonia, has been precipitated at the same time.

* A bar of METALLIC ZINC plunged in a muriatic solution of antimonic acid precipitates antimony, though incompletely, under the form of a black powder.

* Before the BLOW-PIPE antimonic acid behaves like *antimonious acid*, into which the first action of heat converts it.

* The orange-yellow precipitate produced by sulphuretted hydrogen in the acid solutions of antimonic acid easily distinguishes it, and precludes the possibility of confounding it with any other substance, except, perhaps, other degrees of oxydisation of antimony. I shall point out, in treating of

antimonious acid, how it may be distinguished from such other compounds.

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[1] With antimoniates of copper, of zinc, and of cobalt especially, a low red heat is often sufficient to produce this phenomenon, which, though resembling it, is not a true combustion, since the weight of the substance remains unaltered. The same phenomenon has been noticed whilst treating of chloric acid and of zirconia.—ED.

Non-volatile ORGANIC SUBSTANCES, especially tartaric acid, prevent the muriatic solution of antimonic acid from being precipitated by water, by the pure and the carbonated alkalies. But their presence does not hinder the production of the orange-yellow precipitate by sulphuretted hydrogen.

2°. ANTIMONIOUS ACID, SbO_4.

(*Acide Antimonieux*).

* PURE antimonious acid is white. It takes, however, a faint yellow tinge when heated, but this tinge vanishes by cooling, and the mass again becomes white. It may be ignited both in closed or in open vessels, without being fused, or otherwise altered or volatilised. Hydrated antimonious acid is white also.

* Antimonious acid and its hydrate are insoluble in water; soluble, but with difficulty, in muriatic acid, with the help of heat. This solution, like that of antimonic acid, becomes turbid when water is added[1]. Antimonious acid is insoluble in nitric acid.

* In the dry way, antimonious acid expels carbonic acid from the fixed alkaline carbonates, with which it is fused.

* Ignited as well as hydrated antimonious acid reddens litmus paper, when, after being spread upon it, they are moistened with water.

* Antimonious acid forms, with the bases, combinations which have much resemblance with those produced by antimonic acid. Wherefore, the muriatic acid solution of antimonious acid behaves with solutions of PURE and CARBONATED ALKALIES like that of antimonic acid in muriatic acid. Antimonites, like antimoniates, are decomposed by nitric acid, which dissolves the base and leaves the antimonious acid. When, however, these salts have been ignited, an operation which is often accompanied by a disengagement of light similar

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[1] See note, page 301.

to that observed during the ignition of the antimoniates, they are no longer decomposable by nitric acid. The alkaline antimonites do not exhibit this phenomenon during their ignition, and they are decomposable by acids, even after ignition[1].

* Solution of SULPHURETTED HYDROGEN or a current of this gas produces, in the muriatic acid solution of antimonious acid, a precipitate which has the same colour as that produced by the same re-agent in the muriatic acid solution of antimonic acid.

* HYDROSULPHURET OF AMMONIA behaves with antimonious as with antimonic acid.

* The reaction of METALLIC ZINC likewise is the same.

* When antimonious acid is heated in the interior flame of the BLOW-PIPE upon charcoal, it (the charcoal) becomes covered with a white fur, but the metallic antimony does not appear unless the antimonious acid be mixed with soda[2].

* The orange-yellow precipitate which sulphuretted hydrogen produces in acid solutions of antimonious acid distinguishes it from all other substances; oxyde of antimony and antimonic acid excepted. In the pure state antimonious acid differs from oxyde of antimony not only by being less soluble in muriatic acid, but also and especially because, when exposed to heat, it is neither fused nor volatilised. It is distinguished from antimonic acid by its white colour, and because it does not yield oxygen gas when ignited in a small retort.

* It is more difficult to distinguish antimonites from antimoniates. It is necessary to decompose them by muriatic acid, or in the cold, by nitric acid, an operation during which the base ordinarily dissolves in the acid, and the operator next examines whether the remaining acid, being first dried, yields oxygen gas or not, by igniting it in a small retort. Yet when antimonites have been ignited so that they are no longer decomposable by acids, it is still more difficult to know whether

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[1] This phenomenon seems to be dependant upon the passage from an isomeric state to another, that is to say, the passage of the soluble acid into the insoluble modification.—ED.

[2] The metal cannot be obtained in globules without soda, because the metal so reduced in the interior flame is immediately volatilised as fast as it is reduced.—ED.

they contain antimonious or antimonic acid. It is necessary to fuse them in a silver crucible with an excess of hydrate of potash, to treat the fused mass by water, and an acid being added in order to decompose the salt of potash thus dissolved, to examine whether this acid has precipitated antimonious or antimonic acid.

* Non-volatile ORGANIC SUBSTANCES, especially tartaric acid, prevent water and alkalies from precipitating antimonious acid from its solution in muriatic acid, precisely as is the case with the muriatic acid solution of antimonic acid; but they do not prevent the production of the orange-yellow precipitate by sulphuretted hydrogen. When a solution of tartaric acid is mixed with a muriatic acid solution of antimonious and of antimonic acid, and the mixture evaporated, a jelly is obtained on cooling, but no crystals of tartar emetic, as is the case when, after having dissolved in muriatic acid even a very minute quantity of oxyde of antimony, or of a body containing oxyde of antimony, a solution of tartaric acid is mixed with the liquor, and the whole evaporated at a gentle heat. By this character oxyde of antimony may be easily distinguished from antimonious and antimonic acid.

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* The French edition has the following addition by E. Peligot:—

All the combinations of antimony which are soluble in water or in acid disengage antimonietted hydrogen when in contact with nascent hydrogen. This gas is decomposable by heat, and produces metallic antimony in an extreme state of division, by imperfect combustion in the air. In treating of arseniuretted hydrogen, with which antimonietted hydrogen might be confounded, the distinctive properties of this gas will be indicated.—E. P.

14. MOLYBDIC ACID, MoO_3.

(Acide Molybdique.)

* MOLYBDIC acid either forms a white mass, or else acicular crystals of a silky lustre. Heated in close vessels, it fuses and is resolved into a yellow liquid, which after cooling is of a light-yellow colour and crystalline appearance. Heated in the open air, it smokes and sublimes at even a moderate temperature; the sublimed acid forms long shining crystals or spangles.

* Molybdic acid is very sparingly soluble in water[1]. The aqueous solution feebly reddens litmus paper. When the acid is spread upon litmus paper and moistened thereon, the paper is strongly reddened.

* Molybdic acid is very soluble in solutions of PURE ALKALIES and of ALKALINE CARBONATES; but in the latter carbonic acid is disengaged with effervescence. Its combinations with the earths and metallic oxydes are either sparingly soluble or insoluble; wherefore the neutral compounds of earthy salts produce precipitates in those of the molybdates of alkalies. This effect is produced even in acid solutions of molybdates of alkalies, in which a solution of NITRATE OF LEAD determines a white precipitate, and a solution of SUBNITRATE OF MERCURY an immediate yellowish precipitate, insoluble in a large quantity of water, but soluble in a sufficient quantity of nitric acid.

* A neutral solution of a PERSALT OF IRON produces in these solutions a yellowish precipitate soluble in a large quantity of water.

* A solution of NITRATE OF SILVER produces a white precipitate soluble in a large excess of water, but more soluble still in nitric acid and in ammonia.

* The precipitates which CHLORIDE OF BARIUM or CHLORIDE OF CALCIUM produce in solutions of the acid molybdates of alkalies are white, and soluble in a large quantity of water, especially the precipitate produced by chloride of calcium. If,

however, a little ammonia be poured in these solutions, so as to saturate the free acid, a turbidness and a precipitate are produced, insoluble in any excess of water. These precipitates are soluble in a sufficient quantity of nitric or of muriatic acid.

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[1] 570 parts of water dissolve only 1 of molybdic acid.—ED.

* MURIATIC ACID OR NITRIC ACID produce in solutions of molybdates of alkalies, when not too dilute, white precipitates which are soluble in an excess of acid, even in a large quantity of water; consequently, when the solution of the molybdate of alkali is very dilute, the above-named acids form no precipitate. OXALIC, TARTARIC, ACETIC, and SULPHURIC ACIDS produce no precipitate even in pretty concentrated solutions of molybdates of alkalies; often, however, muriatic acid produces in these solutions a precipitate which is re-dissolved by an excess of oxalic or of tartaric acid.

* Molybdic acid itself is easily dissolved by acids, but it generally possesses this property only when it has not been heated to incipient fusion. After ignition it is insoluble in most acids, but the *acid tartrate of potash* dissolves the fused molybdic acid when boiled in water in conjunction with it.

* When a solution of FERROCYANURET OF POTASSIUM is mixed with solution of molybdic acid in muriatic acid, or with the aqueous solutions of the molybdates to which a free acid has been added, and preferably muriatic acid, a brownish-red precipitate is formed, soluble in ammonia, with which it produces a slightly-coloured liquid.

* Solutions of FERRICYANURET OF POTASSIUM determine likewise a brownish-red precipitate having a lighter tinge, which also gives a slightly-coloured solution with an excess of ammonia.

* The aqueous solution of SULPHURETTED HYDROGEN poured in that of molybdic acid, and that of the molybdates to which muriatic acid has been added, produces a brown precipitate of sulphuret of molybdenum, and the supernatant liquid is green. If the molybdic acid is in very small quantity, the solution of sulphuretted hydrogen in excess produces only a green liquid, in which a brown precipitate is formed after long standing, but more rapidly by application of

heat, a circumstance which takes place also if the solution contains much molybdic acid. A current of SULPHURETTED HYDROGEN acts in the same manner when passed through the liquor long enough to saturate it completely. It is, however, very difficult to precipitate all the molybdenum in the state of brown sulphuret so that the liquid filtered therefrom be perfectly colourless. Ordinarily it has a faint greenish or bluish colour, or contains still slight traces of molybdenum. When, on the contrary, to a solution of molybdic acid or of an alkaline molybdate a very small quantity only of aqueous solution of sulphuretted hydrogen is added, so that the liquor does not smell of the gas, a blue liquid is obtained; by a larger addition of aqueous solution of sulphuretted hydrogen, the liquor, besides being blue, yields a brown precipitate; it is only when an excess of solution of sulphuretted hydrogen has been employed that the phenomena above related are produced. An excess of aqueous solution of sulphuretted hydrogen produces no precipitate in acid molybdates of alkalies; the liquor only becomes of a golden-yellow colour. The precipitation of the sulphuret of molybdenum takes place only when muriatic acid is added.

* HYDROSULPHURET OF AMMONIA poured in solutions of molybdates of alkalies, at first produces no change, but after some time, the liquor becomes of a golden-yellow colour. The diluted acids produce therein a brown precipitate of sulphuret of molybdenum.

* The molybdates of alkalies ignited with sal ammoniac, produce a blackish-brown oxyde of molybdenum, which, however, may often contain metallic molybdenum (page 189.)

* A bar of METALLIC ZINC plunged in a muriatic acid solution of molybdic acid, or in the solution of a molybdate of alkali to which an excess of muriatic acid has been added, reduces the molybdic acid to the state of molybdous oxyde, which remains dissolved in the muriatic acid, owing to which the liquor assumes a deep blackish-brown colour.

* The reduction of molybdic acid into molybdous oxyde is not suddenly effected; wherefore the first action of the zinc upon

the liquor is to render it blue, then green, and lastly of a very dark-brown colour.

* TIN behaves in the same manner.

* PROTOCHLORIDE OF TIN poured in the solution of a molybdate of alkali, produces an immediate bluish-green precipitate which dissolves in muriatic acid, and which thus forms a limpid green liquid.

* When, after having added muriatic acid to the solution of a molybdate of alkali, it is boiled with molybdenum, molybdous or molybdic oxyde, a liquid of a fine deep-blue colour is obtained, which is a solution of molybdate of deutoxyde of molybdenum in muriatic acid. The easiest way to obtain this blue liquor with the solution of a molybdate of alkali, consists in pouring an excess of muriatic acid in the latter solution, and in plunging a bar of zinc or of tin in a small quantity of the liquid. After having withdrawn the metallic bar, the solution containing the deep brownish-black protoxyde of molybdenum, is to be mixed with the portion of the molybdate of alkali which has not been reduced. If there has not been sufficient muriatic acid, the liquor will not only be blue, but a precipitate of the same colour will be obtained also. By boiling the liquor with solution of potash, the blue liquor disappears, a dark-brown precipitate of deutoxyde of molybdenum is deposited, and the alkali combines with the molybdic acid.

* Before the BLOW-PIPE, molybdic acid behaves towards microcosmic salt and borax like protoxyde of molybdenum (page 188.)

* The behaviour of solutions of molybdic acid towards muriatic acid and nitric acid solutions, and the reaction of sulphuretted hydrogen in acid solutions, the blue liquor produced in the manner above mentioned, and the phenomena produced by the blow-pipe, render it easy to detect molybdic acid in its soluble compounds, and preclude the possibility of confounding it with any other substance.

* As to its combinations with most metallic oxydes, it may be separated by converting these metallic oxydes into insoluble

metallic sulphurets by dissolving the compounds in acids, saturating with ammonia, and adding hydrosulphuret of ammonia. The presence of molybdenum may be easily detected in the solution by adding a dilute acid thereto; a sulphuret of molybdenum is precipitated and collected on a filter; the precipitate being dried and ignited in contact with the air, the sulphur is burnt away, and molybdic acid formed.

15. TUNGSTIC ACID, WO_3.

(*Acide Tungstique.*)

* TUNGSTIC acid has a yellowish colour, which becomes lemon-yellow by the action of heat. It is frequently obtained under the form of a greenish powder. It is not volatilisable by heat, nor soluble in water. When moistened and placed upon blue litmus paper, it very distinctly reddens it. Acids do not dissolve it.

* With alkalies tungstic acid forms salts which are soluble in water. After ignition it is soluble in the solutions of pure alkalies and of alkaline carbonates; the solution, however, is effected with difficulty, even with the help of heat; at least it is much more difficultly soluble than ignited molybdic acid. When tungstic acid is treated by solutions of alkaline carbonates, there is a disengagement of carbonic acid gas, but the effervescence is not readily observable.

* Many acids produce precipitates in solutions of tungstates of alkalies; MURIATIC, NITRIC, and SULPHURIC ACIDS produce white precipitates. The precipitates produced by muriatic and nitric acids acquire a yellowish colour shortly after being deposited, and more rapidly still with the help of heat; but the precipitate produced by sulphuric acid remains white a longer time, and becomes less yellow when heated. These precipitates are not soluble in an excess of the acid which formed them, which character distinguishes them from those which acids produce in molybdates of alkalies. None of the three acids just named completely precipitate tungstic acid. PHOSPHORIC ACID produces in solutions of tungstates of alkalies a precipitate which

is soluble in an excess of the re-agent. OXALIC ACID and some other non-volatile organic acids, such as TARTARIC and CITRIC ACID, form no precipitates; ACETIC ACID, on the contrary, produces a precipitate which is insoluble in an excess of the re-agent, and which time does not render yellow.

* All the combinations of tungstic acid with the earths and the metallic oxydes appear to be insoluble in water, except, perhaps, *tungstate of magnesia*[1]; wherefore the solutions of earthy and metallic salts produce precipitates in those of tungstates of alkalies. The solutions of CHLORIDE OF BARIUM, CHLORIDE OF CALCIUM, NITRATE OF LEAD, NITRATE OF SILVER, produce white precipitates which are not soluble in a large quantity of water. The combinations of tungstic acid are decomposed by nitric acid, or by other acids; the base dissolves, whilst the tungstic acid separates, but not completely. Several of these combinations of tungstic acid are only incompletely decomposed by acids. The best method of effecting their complete decomposition, when the base is insoluble in alkaline carbonates, consists in fusing the tungstate with about three parts of carbonate of potash or of soda, in a platinum crucible; if the fused mass be now treated by water, the base remains undissolved, whilst the alkaline tungstate produced is taken up; it is then easy to recognise the existence of tungstic acid in the solution.

* The solution of SULPHURETTED HYDROGEN scarcely creates a cloudiness in that of the tungstates of alkalies in some acids; for example, in phosphoric acid.

* HYDROSULPHURET OF AMMONIA does not at first produce any change in the solutions of a tungstate of alkali, but if dilute muriatic acid be added, a light-brownish precipitate of persulphuret of tungsten is formed, the colour of which is clearly seen only when the whole has been at rest for some time.

* When the solution of a tungstate of alkali is supersaturated by an acid, if a bar of METALLIC ZINC be plunged either in the precipitate which is thus produced, but without separating it

from the liquor, or in the solution, if the acid has re-dissolved the precipitate, a fine blue colour of tungstate of oxyde is produced. Zinc produces a finer blue colour in the solution of a tungstate of alkali in an excess of phosphoric acid, or in the precipitate produced by acetic acid, than in the precipitate formed by sulphuric or muriatic acid. A bar of metallic zinc produces no blue colour in the precipitate which sulphuric acid has produced in the solution of a tungstate of alkali, nor in the tartaric or citric acid solutions of tungstates of alkalies, but the blue colour is produced in the solution of these salts in oxalic acid.

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[1] Berzelius says, that tungstate of magnesia is easily soluble in water, and crystallises in shining spangles unalterable in the air.—ED.

* Before the BLOW-PIPE tungstic acid behaves like oxyde of tungsten (page 192).

* The behaviour of tungstic acid before the blow-pipe, and the reactions which its compounds produce with acids and with zinc, do not allow of its being confounded with other substances, except *titanic acid* only; but it is distinguished from the latter acid by the solubility in water of its combinations with alkalies[1], and by the behaviour of its solutions towards acids.

16. VANADIC ACID, VO_3.

(*Acide Vanadique.*)

* VANADIC acid, obtained by heating vanadiate of ammonia in the air, forms, according to Berzelius, a powder which, following its degree of division, is of a brick-red, or of a rusty colour; the more it is triturated the lighter the colour becomes. At an incipient red heat it fuses without decomposition, if the presence of bodies which might reduce it is avoided. On cooling it forms a mass of aggregated crystals. So much caloric is liberated during this crystallisation, that the mass which had cooled below redness becomes luminous again. The mass is very shining, of a red colour, inclining to orange, and the thin edges are translucid. When vanadic acid is fused before complete oxydisation, and consequently when it contains still some oxyde of vanadium, it does not crystallise, but at the instant of its solidification

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[1] The alkaline titanates are almost insoluble in water.—ED.

it produces excrescences like those of a cauliflower, and after cooling the mass is black. This acid presents also the same phenomenon when it contains metallic oxydes. A very minute quantity of oxyde of vanadium does not hinder the crystallisation, but the solidified mass has a darker colour, inclining to violet.

* Vanadic acid is not volatile; it is very sparingly soluble in water, owing to which the solution has no taste. The acid, however, reddens the moistened litmus paper on which it is placed. Reduced to powder and mixed with water, it remains suspended in it, so as to produce a kind of emulsion of a yellowish milky colour, which clears up only very slowly, as water in which clay has been stirred. In this state of division it has, after being dried, a fine yellow colour, absolutely like the hydrate of peroxyde of iron, which is formed under water at the surface of metallic iron. The liquor produced has a pure yellow colour, is tasteless, reddens litmus paper, and after evaporation to dryness leaves scarcely a thousandth part of its weight of vanadic acid.

* Vanadic acid is insoluble in pure alcohol, but is slightly soluble in aqueous alcohol. In the humid way it is easily reduced into oxyde of vanadium, especially when united with another acid. Even *nitrous acid* is oxydised at its expense; for when red fuming *nitric acid* is mixed with a solution of vanadic acid the liquor soon becomes blue. Many metals reduce it to the state of oxyde of vanadium; an effect which is also produced by *sulphurous, oxalic, citric,* and *tartaric acid,* the *oxysalts of several metals, sugar, alcohol, &c.*

* Vanadic acid has much analogy to molybdic and tungstic acids in this sense: that it acts as a base towards the powerful acids, whilst, on the contrary, it behaves towards bases like a strong acid.

* The solutions of vanadic acid in acids are red or of a lemon-yellow colour, but sometimes also they are colourless. When acids are exactly saturated by vanadic acid, these solutions become turbid by ebullition or evaporation, and deposit precipitates of a reddish-brown colour, and which are basic salts.

By long exposure to the air these solutions often become gradually green, which may depend on the dust flying about in the air, and by which they are reduced.

* Treated by MURIATIC ACID vanadic acid disengages chlorine, wherefore its solutions in this concentrated acid become green after some time, and dissolve gold and platinum. The liquid and volatile chloride of vanadium has a light-yellow colour, and dissolves well in water, to which it communicates a feeble yellowish tinge; but in a few days the liquor disengages chlorine, and becomes green, and then blue.

* A solution of FERROCYANURET OF POTASSIUM produces in solutions of vanadic acid in acids a green flocculent precipitate, insoluble in acids.

* HYDROSULPHURET OF AMMONIA imparts a brown colour, similar to that of beer, to the solutions of vanadic acid; if the solution was acid from the presence of another acid, or if to the beer-brown solutions either muriatic or dilute sulphuric acid be added, a brown precipitate of sulphuret of vanadium, of a lighter tinge than that which is produced in similar circumstances in solutions of oxysalts of vanadium. The acid liquor generally becomes blue during this precipitation[1]. The brown precipitate is soluble in an excess of hydrosulphuret of ammonia, and also in solutions of pure alkalies, and of alkaline carbonates.

* SULPHURETTED HYDROGEN produces in solutions of vanadic acid a greyish-brown precipitate, which is simply a mixture of hydrate of oxyde of vanadium and of sulphur.

* INFUSION OF GALLS gives after some time a bluish-black precipitate in the neutral solutions of vanadic acid in acids.

* Almost all the salts which vanadic acid forms with the bases are soluble in water, yet some of them are very sparingly so, though not altogether insoluble; such are, for example, the vanadiates of baryta and of lead. The vanadiates of alkalies are sparingly soluble, especially when the water is alkaline, or when it contains salts in solution. Vanadiate of ammonia, for

example, is insoluble in a solution of muriate of ammonia. Most vanadiates are insoluble in alcohol.

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[1] This blue colour is due to the decomposition of a small quantity of the sulphuret of vanadium in the nascent state.—ED.

* The vanadiates of a same base may be obtained variously coloured, and at several degrees of saturation. The acid vanadiates are always of an orange-red colour; some of them are yellow only, which variation, however, is ordinarily dependant on the size of the crystals, the largest crystals being red. Some of the neutral vanadiates are either colourless or of a deep yellow, which colour appears to be the primary colour of the salts, for nearly all the bases yield, with vanadic acid, neutral salts of a more or less pure yellow colour; yet some of the strongest bases, namely, all the alkalies, all the alkaline earths, the oxydes of zinc, cadmium, lead, and silver, give colourless salts also, the neutrality of the salts remaining unchanged. Ordinarily the yellow salt is decolorised by heat; at a higher temperature, which is yet below the boiling point of water, it rapidly loses its colour and becomes colourless; this effect is produced whether it be its solution that is thus submitted to heat, or a liquid in which it is immersed. Some of the salts likewise spontaneously lose their colour without being heated, when abandoned for some time, especially when they contain an excess of base,—a circumstance which is necessary to the production of the decolorising phenomenon,—although this excess be not in a state of combination with the salt, and may consist of an alkaline carbonate, or of a pure alkali.

* The vanadiates have no particular taste referrible to the acid. When they are mixed with an acid they turn red, but this colour often disappears after some time.

* Like molybdic and tungstic acid, vanadic acid forms, with deutoxyde of vanadium, combinations which are soluble in water, and some of which have a purple or red colour; others are green or orange-yellow. These combinations are sometimes produced by the oxydisation of deutoxyde of vanadium in the air; at other times they result from the immediate union of the acid with the oxyde in the dry or in the humid way.

* Before the BLOW-PIPE vanadic acid behaves in the following

manner:—Alone upon charcoal it fuses, and is reduced at the point where it is in contact with the charcoal, into which the reduced portion penetrates and is fixed, but the greatest part remains on the charcoal, with the colour and shining appearance of graphite, in the state of suboxyde of vanadium. Vanadic acid dissolves in borax and microcosmic salt, in the exterior flame, forming a yellow glass, which in the interior flame becomes of a fine green, similar to the green-coloured bead produced by chrome. When, however, the colour of the bead is intense, it appears brownish whilst it is as yet hot, and the fine green colour appears only after cooling. The most distinctive character of vanadium from chrome before the blow-pipe consists in this: that the green bead produced by vanadium turns yellow in the exterior flame, and that when the combination of vanadium is not abundant, it may be obtained perfectly colourless. Vanadic acid fuses with soda, and penetrates into the charcoal.

* Vanadium has in its combinations much analogy with the corresponding combinations of uranium, of molybdenum, tungsten, and especially of chromium.

* Chromium is the substance with which it is more liable to be confounded. The combinations of these two metals, when treated before the blow-pipe with borax, or with microcosmic salt, communicate to the glass obtained the same green colour; but they may, however, be distinguished from each other by the characters which have been mentioned above. Both chromium and vanadium produce acids of a red, and salts of a yellow colour, but the solutions of which turn intensely red by the addition of an acid. Yet the solutions of the chromates of alkalies retain their colour when heated, whilst the solutions of the vanadiates of alkalies are decolorised when thus treated. Chromic acid is very soluble in water, and has a strong acid flavour; vanadic acid is very sparingly soluble in water, unless it contains deutoxyde of vanadium, in which case the liquor has a green colour, owing to the sparing solubility of vanadic acid in water; the solution, although of a yellow colour, is tasteless. Chromic acid being exposed to a red heat loses oxygen, and is

converted into oxyde of chromium, which is not the case with vanadic acid. Chromic oxyde is green, and insoluble in alkalies; it does not absorb oxygen when exposed to a red heat, and does not dissolve in water; vanadic oxyde is green also when it contains vanadic acid, but it is then soluble in water and in alkalies; and, besides, it absorbs oxygen when exposed to a red heat.

* Vanadium resembles uranium, because there is a green and a yellow oxyde of uranium; and because the behaviour of both substances before the blow-pipe is the same; but the solutions of the yellow sesquioxyde of uranium in acids, which solutions are yellow, are precipitated yellow by the alkalies; the precipitate does not change colour when heated, which constitutes a difference with vanadic acid; the latter, when mixed with an excess of ammonia, being decolorised by heat, and when mixed with sal ammoniac, depositing a white powder of vanadiate of ammonia. It is true that the solutions of sesquioxyde of uranium are not precipitated by solution of carbonate of ammonia, when a great excess of the latter is employed, but they are ultimately precipitated by a prolonged ebullition, which does not happen to solution of vanadic acid. Lastly, the solutions of peroxyde of uranium give a reddish-brown precipitate with that of ferrocyanuret of potassium, whilst the solution of vanadic acid produces a green precipitate with this re-agent.

* Molybdenum has some analogy with vanadium, because both can form compounds, the solutions of which are blue. Yet the blue solutions which molybdenum forms lose their blue colour, and become decolorised when boiled with a solution of potash, molybdic oxyde being deposited at the same time. On the contrary, the alkalies produce in the blue solutions of vanadic oxyde a greyish-white precipitate; and when there is an excess of re-agent, the supernatant liquor is brown.

* Tungsten also may sometimes produce solutions of a blue colour; but in other respects vanadium has not much analogy with it, and is sufficiently distinguished by its behaviour before the blow-pipe.

17. CHROMIC ACID, CrO_3.

(*Acide Chromique.*)

* Pure chromic acid is a powder of a brownish-red colour, or in the form of red, lanuginous, bulky crystals[1]. Exposed to a red heat upon a platinum foil, it is decomposed, disengages oxygen, and leaves oxyde of chromium, which, at a red heat, spontaneously and suddenly becomes ignited throughout (page 195); when chromic acid has been obtained by the evaporation of its solution in water, the disengagement of light does not take place. Chromic acid dissolves in small quantity in water; the solution has a deep-brown colour, and it destroys paper and other organic substances[2]. Like concentrated sulphuric acid, chromic acid is also soluble in alcohol, but in such a solution it soon undergoes decomposition. Treated by boiling concentrated sulphuric acid, it is converted into oxyde of chromium, which dissolves in the acid with disengagement of oxygen gas. Diluted sulphuric acid does not produce this effect.

* Chromic acid forms with the alkalies, salts which are soluble in water. The alkaline chromates are yellow, and the acid chromates are red. The aqueous solutions of these salts have the colour of the salts themselves. When an acid is poured in the yellow solutions of the neutral chromates, the liquor assumes a red colour, because an acid chromate of alkali is thereby formed. This effect takes place at first, when muriatic acid is added, but after a short time it decomposes the chromic acid. With most earths, and a great number of metallic oxydes, chromic acid forms compounds which are insoluble in water, and often also in dilute acids: these compounds are ordinarily of a yellow or red colour. Several insoluble yellow chromates acquire, in passing to the state of basic chromates, a red colour, similar to that of the acid chromates; such is the case, for

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[1] The crystals of chromic acid are deliquescent.—Ed.

[2] The aqueous solution of chromic acid stains the skin yellow, which cannot be washed away by water, but which a solution of alkali removes.—Ed.

example, with the precipitate of chromate of lead, the yellow colour of which turns red by addition of ammonia. Chromic acid forms no acid salts with the earths, nor with the metallic oxydes. As the chromates of alkalies are often resorted to as re-agents for detecting several bases, the behaviour of these bases with chromate of potash has been indicated in the preceding pages.

* When the chromates of weak bases are exposed to a red heat, the chromic acid is reduced to the state of oxyde of chromium, with disengagement of oxygen gas. The excess of acid of the persalts of alkalies undergoes also this change; but the heat must be very strong. The neutral chromates of alkalies are not altered.

* CONCENTRATED SULPHURIC ACID, with the help of heat, disengages oxygen from the chromates. The chromic acid becomes converted into oxyde of chromium, or into chromate of oxyde of chromium.

* The solutions of the chromates, like that of chromic acid, are decomposed by MURIATIC ACID. In the cold, and in a dilute solution, this decomposition is effected very slowly; but with the help of heat, and in a concentrated solution, the decomposition is much more rapid; yet some time must elapse before it is complete. At first, if the salt of alkali be neutral, the liquor reddens, as it does when any acid is added; then chlorine is disengaged, and oxyde of chromium is formed, which, remaining dissolved in the excess of muriatic acid, gives a green colour to the liquor. The decomposition is complete only when the solution has ceased to evolve the smell of chlorine, when it behaves towards re-agents like a solution of oxyde of chromium (page 196). If the chromate contains sulphuric acid, the presence of this acid can be detected by means of a barytic salt, only after the decomposition of the chromic acid by muriatic acid[1]. When alcohol, or other organic substances, are poured into the solution of a chromate to which muriatic acid has

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[1] Solutions of barytic salts produce in solutions of chromate a yellowish-white precipitate of chromate of baryta soluble in dilute muriatic and nitric acids.—ED.

been added, the reduction of chromic acid into oxyde of chromium is more rapidly effected; and then, instead of chlorine, muriatic ether is disengaged[1].

When concentrated MURIATIC ACID is poured upon soluble or insoluble chromates, in a tube of white glass closed at one end, and the whole is afterwards heated, chlorine gas is disengaged, which may be recognised as such by its peculiar colour and its odour.

* If, an acid (for example, nitric or dilute sulphuric acid, but not muriatic acid), being poured in the solution of a chromate or of chromic acid, an excess of aqueous solution of SULPHURETTED HYDROGEN be added, or a current of this gas be passed through the liquor, it changes colour, and ultimately becomes green; the chromic acid being converted into oxyde of chromium, which remains dissolved in the acid employed[2]. After a time sulphur begins to be deposited, which gives the liquor a milky appearance. When the whole is heated for some time, the reduction of the chromic acid into oxyde of chromium, with separation of sulphur, is effected with more rapidity. It is easily conceived, that it is necessary that the liquid should not contain any metallic oxyde susceptible of being precipitated by sulphuretted hydrogen from an acid solution in the state of metallic sulphuret. The liquid, which is separated by filtering from the sulphur deposited, behaves afterwards towards re-agents like a solution of oxyde of chromium. When the chromic acid contained in a solution is reduced in the state of oxyde of chromium by means of sulphuretted hydrogen gas, the sulphur which is separated forms an inconsiderable precipitate, but a great quantity of sulphuric acid is produced.

* When an acid (for example, dilute sulphuric acid) is poured in the solution of a chromate, and a SULPHITE is subsequently

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[1] The evolution of muriatic ether takes place only of course when alcohol has been added, and the ether thus disengaged is mixed with *aldehyde*.—ED.

[2] If enough acid has been employed, the whole of the oxyde of chromium produced is dissolved, and no precipitate except of sulphur is formed; but if there is not enough free acid present, a greenish precipitate of oxyde of chromium will be deposited, mixed with the sulphur.—ED.

added, if the chromate is in sufficient quantity no sulphurous acid is formed, but the chromic acid is converted into oxyde of chromium, which imparts a green colour to the liquor. The reduction of the chromic acid into oxyde of chromium is more easily effected by sulphurous acid than by muriatic acid, and by sulphuretted hydrogen.

* A bar of METALLIC ZINC plunged in the solution of a neutral chromate, and even in that of an acid chromate, produces no change; but if a little dilute sulphuric acid be added to the solution, the liquor assumes a green tinge, due to the transformation of chromic acid into oxyde of chromium.

When the soluble or insoluble chromates are triturated with chloride of sodium, and having introduced the mixture into a tube of white glass closed at one end, concentrated sulphuric acid is poured upon it, and the whole is heated, a frothy effervescence is produced, due to a disengagement of a red gas, which fills the empty space in the tube, and which condenses into a brownish-red liquid, which is a combination of chromic acid and chloride of chromium. If for the chloride used in the mixture a bromide is substituted, a gas is obtained which has almost the same colour, and which condenses also into a brownish-red liquid; but which is pure bromine[1].

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[1] The solutions of the salts of lead, for example, the nitrate and acetate of lead, determine in solution of chromates a fine yellow precipitate of chromate of lead soluble in caustic potash, and to some extent in nitric acid. The addition of ammonia, especially with the help of heat, converts it into subchromate of lead, which has an orange-red colour. The insoluble chromates, or substances containing chrome, which are insoluble, may be tested for chrome in the following way:—They are to be well pulverised and mixed with about three times their weight of nitrate of potash, or of nitrate of potash mixed with carbonate of soda, and calcined at a bright red or white heat in a well-covered hessian crucible for about two hours. The crucible is to be reduced into coarse powder and digested in boiling water. If any chrome was present, the water will assume a more or less deep yellow tinge, owing to the alkaline chromate held in solution. The addition of a little nitric acid to slight supersaturation produces a clear orange-yellow solution, owing to the alkaline chromate being converted into bichromate. Solution of acetate of lead poured therein produces a bright yellow precipitate of chromate of lead, and heating the yellow solution with muriatic acid and alcohol renders it green, owing to the conversion of the chromic acid into oxyde of chromium. *Nitrate of silver* produces in solution of chromates a purple, or if the solution contain an excess of acid, a carmine red precipitate of chromate of silver soluble in ammonia and in nitric acid.—ED.

Before the BLOW-PIPE the chromic acid of the chromates behaves like oxyde of chromium (page 198).

* Chromic acid has so many properties which are peculiar to itself that it cannot be confounded with any other substance. The facility with which it is reduced into oxyde of chromium soon identifies it, the latter compound being easily detected in solutions (page 198).

* Most organic substances reduce chromic acid into oxyde of chromium, with disengagement of carbonic acid. This reduction is more especially effected in a rapid manner in solutions of chromates by non-volatile organic substances, such as, for example, tartaric or citric acid, principally when they are heated with these substances; carbonic acid is then disengaged with effervescence. Oxalic acid acts also in the same manner. Some very volatile organic acids, such as acetic acid, do not reduce chromic acid in solutions of chromates; other non-acid organic substances, such as sugar, alcohol, &c., reduce the chromic acid in solutions of chromates, but the reduction is only partial, and extremely slow. This reduction takes place more rapidly under the influence of these substances in solutions of the acid chromates; it is easily conceived that in such a case no disengagement of carbonic acid is perceived. But if a few drops of dilute sulphuric acid be added, the reduction is effected in an extremely rapid manner, especially with the help of heat, and carbonic acid is then disengaged with effervescence. The alkalies cannot serve to detect the presence of oxyde of chromium in solutions of chromates the chromic acid of which has been converted into oxyde of chromium by the influence of non-volatile organic substances (page 198).

18. ACIDS OF MANGANESE.

1°. HYPERMANGANIC ACID, Mn_2O_7.

(*Acide Hypermanganique.*)

* According to Mitscherlich, who first recognised that hypermanganic acid was a distinct acid, hypermanganic acid is pre-

pared by dissolving some hypermanganate of baryta in water, and adding to the solution a quantity of sulphuric acid sufficient to precipitate all the baryta in the state of sulphate of baryta[1]. It is a liquid of an intense crimson colour, which has a very strong colouring power, for a very small portion is sufficient to impart a strong crimson tinge to a large mass of water. It cannot be concentrated, because it undergoes decomposition, though very slowly, at the ordinary temperature; but at 30° or 40° Cent. (86° or 104° Fahr.) the decomposition proceeds very rapidly, oxygen gas is disengaged, and [hydrated] peroxyde of manganese is deposited[2]. According to Mitscherlich, hypermanganic acid parts with its oxygen with greater facility still than oxygenated water. Hunefeld says that it may be obtained in a much more stable state by washing the green manganate of baryta with hot water, and pouring thereon a quantity of phosphoric acid sufficient to saturate the baryta. The whole may be heated, an operation which facilitates the separation of the phosphate of baryta produced; the hypermanganic acid left in solution may be decanted and evaporated to dryness, and likewise redissolved without decomposing it; by evaporating it again, it may be obtained in the form of a crystalline mass of a reddish-brown colour.

* Hypermanganic acid forms with all the bases salts which are soluble in water. In the solid state these salts are almost black, or of a very dark reddish-brown colour; when mixed with other bodies easily oxydisable, and thrown upon ignited charcoal, they deflagrate like the nitrates and chlorates. Heated alone the pure hypermanganate of alkalies are converted into manganates and compounds of peroxyde of manganese and of alkali. The solutions of these salts have a very intense purple

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[1] Hypermanganate of baryta is prepared by calcining nitrate of baryta with peroxyde of manganese. The green mass, insoluble in water, which is then obtained is manganate of baryta; being reduced to fine powder and treated by dilute sulphuric acid, it yields a red solution of hypermanganate of baryta, from which, after being concentrated by evaporation, the baryta may be precipitated by a careful addition of sulphuric acid.—Ed.

[2] Solar light has the same decomposing influence.—Ed.

colour, and like the acid most of them have also very strong colouring powers. There are no hypermanganates completely insoluble. The least soluble of all is hypermanganate of silver. Hypermanganate of potash, which is the best known of these salts, is sparingly soluble. Hypermanganate of soda, lime, strontia, magnesia, oxyde of zinc, and protoxyde of copper, deliquesce in the air. Hypermanganic acid cannot combine with oxyde of lead, protoxyde of manganese, nor protoxyde of iron, because it abandons oxygen to these bases, which then pass to a higher degree of oxydisement. The aqueous solutions of hypermanganates are easily decomposed. That of hypermanganate of potash in solution of pure POTASH cannot be evaporated except when placed under the receiver of the air-pump, by the side of a dish of concentrated sulphuric acid. Without this precaution it is gradually decomposed, even in the cold, and more rapidly when heated, producing manganate of potash, which is green, and disengaging oxygen. If the decomposition be slowly effected the quantity of green manganate of potash gradually augments in proportion as that of the red hypermanganate diminishes, and during the phases of this transformation a series of changes of colour is observed, which are due to the mixture of red hypermanganate and of green manganate in different proportions. If an acid be added to the green solution, it becomes red; for, as will be seen further on, hypermanganic acid is then formed, and a brown powder is deposited.

* AMMONIA and the ALKALINE CARBONATES cannot produce the green colour of manganate of potash in the red solutions of hypermanganate of potash; nitrogen gas is evolved, and hydrate of peroxyde of manganese is deposited.

* When NITRIC or SULPHURIC ACID is poured upon the dry hypermanganates, or in the solutions of these salts, and heat is applied, they are decomposed, just as hypermanganic acid itself, into oxygen gas, which is disengaged, and peroxyde of manganese, which falls down in the state of a brown powder.

* When a hypermanganate or hypermanganic acid is treated by MURIATIC ACID, chlorine gas is evolved, even in the cold; with the help of heat, the deutoxyde of manganese which had

separated is dissolved, and chlorine gas is also evolved. The solution is colourless, and contains both protochloride of manganese, and the base of the decomposed hypermanganate, which base is in the state of metallic chloride.

* A solution of SULPHUROUS ACID, or of a SULPHITE, with addition of an acid, decomposes very easily the solutions of hypermanganates, which are thereby decolorised, and sulphate and hyposulphate of protoxyde of manganese are formed.

* PHOSPHOROUS ACID and other reducing acids decompose very rapidly the solutions of the hypermanganates.

* The solution or a current of SULPHURETTED HYDROGEN decolorises immediately the solutions of hypermanganates; sulphuret of manganese of a flesh colour is formed, but so much sulphur is deposited at the same time, that the precipitate appears quite white.

* HYDROSULPHURET OF AMMONIA poured in excess in solutions of the hypermanganates gives a flesh-coloured precipitate of sulphuret of manganese.

* Before the BLOW-PIPE the hypermanganates behave like protoxyde of manganese.

The intense crimson colour of the hypermanganates and of their solutions, the facility with which they are decomposed into oxygen gas and hydrate of peroxyde of manganese, the abundant disengagement of chlorine gas which they produce when treated by muriatic acid, and their behaviour before the blow-pipe is so characteristic that they cannot be confounded with other combinations.

* Almost all ORGANIC SUBSTANCES easily decompose hypermanganic acid; it is reduced by them with disengagement of carbonic acid into deutoxyde of manganese, and even, with the help of heat, into protoxyde of manganese. Vegetable and animal colours are instantaneously destroyed by this acid, and the solutions of the hypermanganates produce also the same effect, but less powerfully. The bleaching is however very rapid when an acid is added. The filtering paper itself has a reducing influence upon hypermanganic acid and the solution

of its salts, so that these liquids are partially decomposed by filtering[1].

2°. MANGANIC ACID, MnO_3.

(*Acide Manganique.*)

* MANGANIC ACID in a state of purity has not as yet been obtained; it is known only in combination with bases. In order to obtain it, a strong base, for example, potash or the nitrates of such bases, are exposed to a red heat in conjunction with peroxyde of manganese. Whether the operation be performed with or without the contact of the air, a manganate is thus produced; with the contact of the air, because the peroxyde of manganese absorbs oxygen from the air, and is thereby transformed into manganic acid; without the contact of the air, because, according to Mitscherlich, the peroxyde of manganese is decomposed into manganic acid and deutoxyde of manganese[2]. By dissolving the mass an intensely green liquid is obtained, which contains manganate of potash, mixed with pure potash and carbonate of potash; there remains a brown powder composed of hydrated deutoxyde and hydrated peroxyde of manganese.

* The manganates in the solid state are so intensely green that they often appear black. Their aqueous solutions are intensely green also; manganic acid is still more easily decomposed in such solutions than hypermanganic acid. All the acids, even the weakest, impart immediately an intense red colour to the green solutions of the manganates, because they convert the manganic into hypermanganic acid, which is accompanied by the formation of a black precipitate of peroxyde of manganese. The hypermanganic acid produced undergoes decomposition,

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[1] In order, therefore, to separate the precipitates from hypermanganic acid, it must be done by decantation, and never by filtering.—ED.

[2] When a nitrate of alkali is used, the result is the same as when air is admitted, because the oxygen of the nitrate converts the peroxyde of manganese into manganic acid. In both cases, that is when the operation is performed with the contact of the air or with a nitrate of alkali, there is always of course a larger quantity of manganic acid produced than when a hydrate of alkali is used or when the air is excluded.—ED.

as we have previously stated, either slowly at the ordinary temperature, or more rapidly by applying a gentle heat.

* Water alone decomposes the solution of manganate of potash as if it were an acid; it reduces it into hypermanganic acid and hydrate of peroxyde of manganese. A solution of pure POTASH is the only menstruum which dissolves it without decomposition. The solution must be evaporated in vacuo; by which means crystals of manganate of potash mixed with hydrate of potash are obtained. If this solution be exposed to the air, the carbonic acid contained in the atmosphere saturates the excess of potash, after which it reacts upon the manganic acid, which it reduces into hypermanganic acid and peroxyde of manganese.

* MURIATIC ACID at first reddens the green solution of a manganate as other acids do, but the red colour disappears soon after, under an abundant disengagement of chlorine gas, and the liquor becomes a dark-brown solution of deutoxyde of manganese in muriatic acid, which solution, upon heat being applied, again disengages chlorine, and is converted into a colourless solution of protochloride of manganese.

* SULPHUROUS ACID and other reducing acids, SULPHURETTED HYDROGEN, and HYDROSULPHURET OF AMMONIA, behave towards the manganates as towards the hypermanganates.

* Before the BLOW-PIPE the manganates behave like protoxyde of manganese. The green colour which is imparted to soda, when it is fused upon platinum foil with manganiferous substances, is owing to the production of manganate of soda.

* The change from green to red, which the manganates and their solutions undergo when treated by diluted acids, and which is due to the transformation of manganic into hypermanganic acid, and the abundant disengagement of gaseous chlorine, which takes place when these salts are treated by muriatic acid, identifies them so well that they cannot be confounded with other salts.

* Manganic acid, in the manganates, is decomposed by almost all ORGANIC SUBSTANCES. It is true that the organic

acids impart a red colour to all the green solutions of the manganates, exactly as all other acids do, and produce hypermanganic acid, but they soon reduce the hypermanganic acid thus formed into deutoxyde of manganese, with disengagement of carbonic acid, or even, if heat be applied, into protoxyde of manganese; the non-acid organic substances, such as sugar, alcohol, &c., destroy very rapidly the green colour of manganates. The addition of dilute sulphuric acid hastens much the reduction of the manganic acid, with disengagement of carbonic acid.

The French edition has the following note by M. E. Peligot:—

FERRIC ACID, FeO_3.

(Acide Ferrique.)

* M. Frémy has obtained a new combination of iron and oxygen by peroxydising iron in presence of potash; *ferric acid* corresponds to manganic acid, and its composition is, therefore, represented by the formula FeO_3.

* Ferrate of potash is prepared in the dry way by projecting two parts of dry pulverised nitrate of potash upon one part of red hot iron turnings. The result is a reddish mass containing a great quantity of ferrate of potash. The same compound is obtained in the humid way by passing a current of chlorine through a very concentrated solution of potash, in which hydrate of peroxyde of iron is held in suspension.

* Ferrate of potash is decomposed by heat, by the contact of organic substances, and by bodies in a fine state of division. Its aqueous solution is violet, and it is decomposed by a large quantity of water into hydrate of peroxyde of iron, oxygen, and potash[1].—E. P.

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[1] In addition to this note of M. E. Peligot, we should say that M. Frémy has since published, in the *Annales de Chimie et de Physique*, xii., page 365, a Memoir upon ferric acid. According to this chemist, ferrate of potash may be advantageously prepared by heating a crucible to redness, introducing therein about 5 grammes (75 gr.) of pure iron turnings, and when these are incandescent to project upon them 10 grammes (150 gr.) of pulverised nitrate of potash previously fused. The

19. OSMIC ACID, OsO_4.

(Acide Susosmique.)

* PURE anhydrous osmic acid forms a white crystalline mass when it has been obtained by oxydising metallic osmium. It is softened by the heat of the hand: at a higher temperature it fuses, and at a higher temperature still it is volatilised, and then condenses into white drops and crystalline needles upon the cold parts of the vessel in which the experiment is performed: placed upon ignited charcoal it is reduced with detonation. Even in the cold it has a very strong pungent and extremely disagreeable odour[1]. Its vapours greatly irritate the nose and eyes. Water dissolves it but slowly. When heated in that menstruum it fuses into drops under the liquid, as is the case when phosphorus is heated under water. The aqueous solution, even in the cold, exhales a strong odour similar to that of the dry acid, and it is colourless and scarcely reddens litmus paper at all, or only very feebly.

* When the aqueous solution of osmic acid is mixed with solutions of pure alkalies, its odour disappears and the liquid becomes yellow. Yellow or brown appears to be the colour of most osmiates. If the acid be dissolved in a great excess of ammonia, the liquor, especially when heated, assumes a deeper tinge after a long time, and ultimately becomes black and opaque; nitrogen gas is then gradually disengaged, and the

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iron deflagrates in a vivid manner, the crucible is then to be covered and suffered to cool. The reddish violet residuum may be easily detached from the crucible, and preserved in a dry phial. It contains a little hyperoxyde of iron, and produces a slight disengagement of gas whilst dissolving in water. To obtain pure ferrate of potash, the red mass is to be dissolved in water, the clear liquor decanted, and a very concentrated solution of hydrate of potash is to be added in sufficient quantity, so as to render the ferrate of potash insoluble in the alkaline liquor, whereupon the ferrate of potash is precipitated in the state of a black powder, which may be deprived of moisture by placing it on a dry brick placed in an exsiccator. The ferrate may now be slightly warmed upon a piece of porous china, and then kept in a glass tube, which is to be sealed with the lamp.—ED.

[1] The odour resembles that of chloride of sulphur, and excites coughing, but is not acid.—ED.

osmic acid is converted into sesquioxyde of osmium (*acide susosmieux*), part of which sticks to the sides of the vessel under the form of a brownish-yellow precipitate.

* When nitric or muriatic acid is poured in solutions of osmiates of alkalies, osmic acid is liberated, which is recognised by its odour, especially when the liquor is heated. An aqueous solution of osmic acid may then be obtained by distilling.

* Free osmic acid, *in a free state*, seems not to afford precipitates with neutral solutions of earthy and of metallic salts, but precipitates appear by saturating it[1]. It does not form precipitates in neutral acetate or nitrate of protoxyde of lead; but if a little ammonia be added, a deep brown precipitate is immediately produced. Free osmic acid produces also an immediate brown precipitate in a solution of basic acetate of lead.

* A solution of PROTOSULPHATE OF IRON reduces osmic acid, and produces a deep black precipitate in its solutions.

* PROTOCHLORIDE OF TIN determines in solutions of osmic acid a brown precipitate, soluble in muriatic acid, with which it produces a brown liquor.

* Most metals, even mercury, precipitate metallic osmium from a solution of osmic acid, when another acid is added[2].

* If a SULPHITE be plunged in a solution of osmic acid, the liquor, even when it contains only a very minute trace of this acid, assumes immediately a deep violet-blue tinge, and a black precipitate of osmium is formed. The liquor in course of time becomes blue, and when left for a long time at rest it becomes decolorised, whilst the black precipitate augments. Though a very large quantity of water be added, the intensity of the blue, or rather violet colour, does not appear to diminish. This violet colour is more permanent in a very dilute than in a concentrated solution.

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[1] The affinity of osmic acid for bases is very feeble. In the humid way it does not displace carbonic acid from carbonates, and heat expels it from its combinations with most bases, except those which it forms with the fixed alkalies, which retain a considerable quantity of osmic acid even after exposure to a red heat.—ED.

[2] From a solution of osmic acid alone, that is unmixed with another acid, the precipitate produced by metals is a mixture of osmium and of osmiate of the metal employed.—ED.

* SULPHURETTED HYDROGEN, either aqueous or gaseous, produces in solutions of osmic acid a brownish-black precipitate, which remains in suspension, and is easily deposited only by adding muriatic or another free acid to the liquor.

* HYDROSULPHURET OF AMMONIA produces in solution of osmic acid, a black precipitate, which is not soluble in an excess of the re-agent.

* The disagreeable odour which free osmic acid exhales is so characteristic that it cannot be confounded with any other substance.

* A very great number of ORGANIC SUBSTANCES reduce the aqueous solution of osmic acid. If alcohol be poured in a solution of osmic acid, no change at first is produced, but after some time, a blue-black precipitate of metallic osmium is formed. If the alcohol is diluted with much water, osmium is not reduced. Acetic acid, at first, does not produce any change in the solution of osmic acid, but after a certain time it becomes of a violet colour[1]. Some organic substances seem to produce no change whatever in the solution of osmic acid, even after a very long time.

20. ACIDS OF ARSENIC.

1°. ARSENIC ACID, AsO_5.

(*Acide Arsenique.*)

* In the pure state arsenic acid forms an opaque mass of a milky-white colour. It attracts moisture from the air, and ultimately deliquesces, but for this a long time is required. In the anhydrous state water dissolves it completely, though slowly; but a large portion remains for a long time undissolved in the state of a white powder[2]. Arsenic which has absorbed

moisture from the atmosphere is easily soluble in water. Solution of arsenic acid strongly reddens litmus paper. Anhydrous arsenic acid fuses at a low red heat into a white mass, which by dissolving it in a small quantity of water, leaves arsenious acid. Exposed to a higher temperature, it is entirely volatilised, but not without decomposition, for it is reduced into arsenious acid and oxygen gas.

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[1] According to M. Frémy, when osmic acid is saturated by concentrated potash, and alcohol is added drop by drop to the solution, the liquor developes heat, it becomes of a slight pink colour, and an abundant crystalline powder is precipitated, composed of sesquioxyde of osmium and of potash, which sesquioxyde (called by M. Frémy *osmious acid*), cannot be separated from an alkali by means of an acid, because it is thereby converted into deutoxyde of osmium and osmic acid $OsO_2 + OsO_4$.

[2] Six parts of cold or two of boiling water are required to dissolve one of arsenic acid.—ED.

* Arseniates, so far as regards their crystalline form, solubility in water, and several other properties, have much resemblance with the corresponding phosphates. The neutral or acid arseniates of alkalies alone are soluble in water. In this respect again, it resembles phosphoric acid. The neutral arseniates of earths and of metals are insoluble in water and dissolve only in an excess of arsenic or other free acids; wherefore solutions of neutral arseniates are precipitated by the neutral solutions of all earthy or metallic salts; these precipitates are soluble in free acids, and when their acid solution is saturated with an alkali, the arseniates are precipitated. Yet it often happens that an excess of alkali, especially of potash, takes up arsenic acid, and the metallic oxyde is thrown down with its peculiar colour; but in this case, as with the corresponding phosphates, it is not possible to free the precipitate completely from its arsenic acid. When the bases of the precipitated arseniate are soluble in an excess of alkali, the arseniate likewise is soluble.

* A precipitate of arseniate of baryta or of lime is produced in solutions of neutral arseniates of alkalies, not only by solutions of CHLORIDE OF BARIUM and of CHLORIDE OF CALCIUM, and of other *earthy salts*, but also by BARYTA WATER and LIME WATER.

These precipitates are soluble in muriatic and in nitric acids, and also in solutions of ammoniacal salts, especially in that of muriate of ammonia. A much less quantity of salt of ammonia is required to dissolve the precipitate of arseniate of baryta or of lime than to dissolve that of phosphate of baryta or of lime. When free ammonia is present, the earthy arseniates are more difficultly soluble in the salts of ammonia; yet it often happens that an excess of ammonia produces no precipitate when added to a solution of arseniate of baryta or of lime, in a very large quantity of muriatic or of nitric acid.

* A solution of NITRATE or of ACETATE OF LEAD produces a white precipitate of arseniate of lead in solutions of arseniates of alkalies. This precipitate differs from the corresponding precipitate of *phosphate of lead* by its behaviour before the blow-pipe. It does not crystallise when fused upon charcoal by the blow-pipe, but the internal flame reduces it in the state of metallic lead, with disengagement of heavy fumes of arsenic accompanied by the odour of garlic[1].

* A solution of NITRATE OF SILVER produces in solutions of arseniates of alkalies a brown precipitate of basic arseniate of silver, which is very soluble in nitric acid and in ammonia. When the precipitate is dissolved in nitric acid, the addition of ammonia causes it to reappear with its characteristic colour, an effect which takes place especially when its ammoniacal solution is saturated by means of nitric acid[2]. The supernatant liquid above this precipitate reddens litmus paper, even though the solution of the arseniate and that of the nitrate employed was neutral. However strongly ignited the arseniate may have been before it is dissolved, this circumstance has no influence upon the colour or the nature of the precipitate.

* A solution of a neutral PROTOSALT OF COPPER, for example, sulphate of protoxyde of copper, produces in the neutral solutions of arseniates of alkalies a pale greenish-blue precipitate of

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[1] The white precipitate of arseniate of lead is soluble in nitric and muriatic acids. If the neutral arseniate be mixed with acetate of lead, the precipitate is a basic arseniate of lead, and free acetic acid remains in the liquor, the affinity of arsenic acid for oxyde of lead being great.—ED.

[2] The solution of arsenic acid is not precipitated like the neutral arseniate by solution of nitrate of silver, because as arseniate of silver is soluble in nitric acid, it is kept in solution by the nitric acid resulting from the decomposition of the nitrate of silver. But ammonio-nitrate of silver produces a brown precipitate of arseniate of silver in solutions of arsenic acid or of an arseniate. This brown precipitate of arseniate of silver is very characteristic.—ED.

arseniate of copper, which is also produced when solutions of phosphates are mixed with protosalts of copper[1].

SULPHURETTED HYDROGEN, either in aqueous solution or in the gaseous state, determines a light-yellow precipitate of persulphuret of arsenic (sulpharsenic acid) in the solution of arseniates to which a free acid has been added, for which purpose a little muriatic acid is preferable. But this precipitate does not at once appear in dilute solutions, and is formed only after standing for a very long time; its production, however, may be hastened by boiling the whole as soon as the sulphuretted hydrogen is in excess. This precipitate is very soluble in hydrosulphuret of ammonia, and in a solution of pure potash or of ammonia, and even in a solution of carbonate of potash or of soda, this property may easily distinguish it from the precipitate produced by sulphuretted hydrogen in solutions of oxyde of cadmium[2].

HYDROSULPHURET OF AMMONIA produces no precipitate in solutions of neutral arseniates of alkalies. When a few drops of this re-agent are poured in a very concentrated solution of an arseniate, a yellow turbidness is indeed produced, but this turbidness entirely disappears by a larger addition of hydrosulphuret of ammonia. If an acid, especially muriatic acid, is then poured in this solution, mixed with hydrosulphuret of ammonia, sulphuretted hydrogen gas is evolved, and, at the same time, a light-yellow precipitate of persulphuret of arsenic (sulpharsenic acid) is produced, which, however, appears in dilute solutions only after some time, but which may be hastened by heat. Persulphuret of arsenic may thus be precipitated with greater facility than from an acid solution by means of sulphuretted hydrogen. This persulphuret fuses, but less readily than sulphur, and sublimes without change, in the form of a crystalline mass.

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[1] Ammonio-sulphate of copper produces also a greenish-blue precipitate of arseniate of copper in neutral solutions of arseniates, and likewise in a solution of free arsenic acid.—ED.

[2] Sulphuretted hydrogen produces no precipitate in alkaline or even in neutral solutions of arseniates. To obtain it a free acid must be present. Moreover, sulphuretted hydrogen does not precipitate arsenic acid so completely nor so readily as arsenious acid; therefore it is often expedient to convert the arsenic acid or the arseniate into arsenious acid, or an arsenite, by adding aqueous solution of sulphurous acid to that of arsenic acid or of arseniate, a portion of the oxygen of the arsenic acid is transferred to the sulphurous acid, which then becomes sulphuric acid, whilst the arsenic becomes arsenious acid. This transposition is greatly promoted by the application of heat, which serves besides to expel the excess of sulphurous acid. If sulphuretted hydrogen be now added, the whole of the arsenic is precipitated with a bright yellow colour in the state of sesquisulphuret of arsenic (sulpharsenious acid). This treatment is often resorted to, because it frequently occurs that a small quantity of arsenic acid contained in a liquor, obstinately resists the decomposing action of sulphuretted hydrogen. This method was first proposed by M. Wöhler.—ED.

* The precipitate which sulphuretted hydrogen produces in the acid solutions of arseniates easily distinguishes arsenic acid from other acids, especially from phosphoric acid which, like arsenic acid, produces, with earths and metallic oxydes, compounds which are insoluble in water. The presence of arsenic acid may escape observation so much the less, that, as will be shown further on, the behaviour of its combinations before the blow-pipe are quite peculiar and characteristic.

* When arsenic acid is combined with earths, or with metallic oxydes, which are not susceptible of being precipitated from their acid solutions by sulphuretted hydrogen, such as for instance, *peroxyde of iron, protoxyde of iron, oxyde of cobalt, oxyde of nickel, oxyde of zinc, protoxyde of manganese, oxyde of uranium, oxyde of chromium,* &c., the combination is to be dissolved in an acid, and preferably in muriatic acid; the solution is to be diluted with water, and a current of sulphuretted hydrogen passed through it to saturation. After a time, a precipitate is then formed, which from its colour and solubility in hydrosulphuret of ammonia may be easily recognised as persulphuret of arsenic, by which means the presence of arsenic acid is positively established. The solubility of the persulphuret of arsenic in ammonia[1] precludes the possibility of confounding it with a precipitate of sulphur.

* When arsenic acid is combined with metallic oxydes which

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[1] Strong caustic ammonia must be employed, for it is only in such ammonia that persulphuret of arsenic is soluble. Diluted ammonia leaves a residuum of sulphur.—Ed.

are precipitable from an acid solution by sulphuretted hydrogen in the state of metallic sulphurets insoluble in hydrosulphuret of ammonia, the compound is to be dissolved in an acid, the solution saturated with ammonia, to which hydrosulphuret of ammonia is to be added, even when the ammonia has determined a precipitate. The persulphuret of arsenic which will have formed is thereby dissolved, whilst the bases with which the arsenic acid was combined remain in the state of metallic sulphurets, which may be collected on a filter. The persulphuret of arsenic must now be precipitated from the filtered liquid by adding diluted muriatic acid thereto, and it is to be separated from the sulphur, which will have been precipitated with it, by re-dissolving it again in ammonia.

* When arsenic acid is combined with metallic oxydes, which are precipitable from their acid solution by sulphuretted hydrogen in the state of metallic sulphurets soluble in hydrosulphuret of ammonia, such as for example, peroxyde of tin, sesquioxyde of antimony, &c., the presence of arsenic acid must be ascertained by means of the blow-pipe, in the manner described further on.

* It is often possible in qualitative analysis to separate from arsenic acid the metallic oxydes which are absolutely insoluble in solution of potash, by resorting to a process similar to that which has been mentioned in treating of phosphoric acid (page 268). It is true that the operator cannot, any more than with the corresponding phosphates, completely separate the metallic oxyde by treatment with potash, but the most part may thus be liberated; hydrosulphuret of ammonia must then be poured in the filtered liquid, which is next to be supersaturated with dilute muriatic acid. The presence of arsenic acid in the combination may be recognised by the precipitate of persulphuret of arsenic produced.

* Arsenic acid is much more easy to detect in its combinations by means of the BLOW-PIPE, than in the humid way, even when only in very minute quantity. Mingled with soda, and heated in the interior flame of the blow-pipe, the garlic odour

which characterises arsenic is developed, and the minutest trace of that metal may thus be detected in arseniates. It is important never to omit treating by soda the compound in which arsenic acid is sought for, before submitting it to the interior flame of the blow-pipe, because when the acid exists only in small quantity, it is the only means by which its presence can be detected.

* Arseniates are not volatile in the fire when this is the case with their base itself. Many of them, especially amongst the acid arseniates, are fusible. Several acid arseniates by being strongly heated lose a portion of their arsenic acid, which, in that case, is decomposed and disengaged in the state of arsenious acid and oxygen gas. When the experiment is performed in a strong glass tube closed at one end, the arsenious acid is deposited in the colder portion of the tube. When the compounds of arsenic acid have been mixed with charcoal-powder, the arsenic acid is decomposed. If they contain an excess of arsenic acid, or if the base with which it is combined is not reducible into the metallic state by charcoal, the result of the calcination with charcoal is metallic arsenic, which deposits in the colder part of the tube. Other combinations treated in this manner yield no metallic arsenic, but are converted into a non-volatile metallic arseniuret. Arseniates mingled with charcoal-powder and boracic acid, and heated in a glass tube closed at one end, produce on the cold part a metallic mirror.

* Arseniates are easily distinguished from all the substances which have been hitherto treated of, by their behaviour before the blow-pipe, and by the deportment of their solutions towards sulphuretted hydrogen and hydrosulphuret of ammonia. The behaviour of arsenic acid towards sulphuretted hydrogen has some resemblance with peroxyde of tin, but it differs greatly from it by its behaviour before the blow-pipe[1]. We shall

indicate further on the process for distinguishing arseniates from arsenites.

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[1] This precipitate may be distinguished also from the precipitate which sulphuretted hydrogen produces in peroxyde of tin, because when heated it sublimes without alteration in a thick viscid mass of a brownish-red colour, which, after cooling, is transparent and reddish-yellow, whilst persulphuret of tin cannot be completely

* In order to detect the presence of arsenic acid or of arseniates mixed with a large quantity of ORGANIC MATTER, the process is the same as for *arsenious acid,* to which substance the reader is referred.

2°. ARSENIOUS ACID, AsO_3.

(Acide Arsenieux.)

* ARSENIOUS acid, as found in commerce, is a white powder, or a white, vitreous, brittle mass, with a conchoidal fracture. It may be obtained in a transparent state, but it becomes opaque and similar to china when left for a long time exposed to the air, though it does not thereby absorb moisture from the air[1]. Crystallised from its aqueous solution, it may be obtained in the form of regular octahedra, which is often also the form of its sublimate.

* When heated, arsenious acid volatilises in the form of white fumes, which have not the odour of garlic, provided it be not in contact, whilst heated, with organic substances capable of effecting its reduction; in the contrary case, it emits an odour of garlic, which odour is exclusively that of the fumes of metallic arsenic. Wherefore, when arsenious acid is heated upon a piece of glass or upon a platinum foil, it volatilises without evolving the odour of garlic, provided it be pure, and perfectly free from metallic arsenic, and does not contain any organic substance, whilst the odour of garlic becomes at once perceptible, when heated upon red-hot charcoal, or a plate of iron. When a large quantity of arsenious acid is exposed to a high temperature in closed vessels, it melts into a transparent glass, an effect which does not take place with the contact of the air.

* Arsenious acid is sparingly soluble in water, but more so in

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sublimed by heat, and becomes converted into peroxyde of tin when kept at a red heat for a sufficient length of time in contact with the air.—ED.

[1] This opacity is probably due to a mechanical change in the mode of aggregation of its molecules, but whether exposed or not to the air, it always becomes opaque in course of time.—ED.

cold than in boiling water[1]. The hot solution deposits, on cooling, anhydrous arsenious acid, in octahedral crystals. The solution of this acid in cold water may be evaporated for a pretty long time without the acid separating. It reddens litmus paper but feebly.

* Arsenious acid is more soluble in most acids than in water, especially with the help of heat. It is not altered by being thus dissolved, for the solution in acids yields, on cooling, octahedral crystals similar to those obtained from a hot aqueous solution. The best solvent of arsenious acid is muriatic acid, which takes up a considerable quantity of it, especially with the help of heat. When the vitreous acid is dissolved in hot muriatic acid, it crystallises, for the most part, on cooling, and the crystallisation is accompanied by a disengagement of light. Diluted hot sulphuric acid dissolves much less arsenious acid than muriatic acid does. Nitric acid dissolves only very small quantities of it, and does not convert it into arsenic acid, even by applying heat. This conversion can be effected only with aqua regia. Acetic acid dissolves only a minute trace of arsenious acid, less even than water[2].

* The solutions of ALKALIES dissolve arsenious acid much more easily than water does. It is also soluble in the alkaline carbonates. Yet when the solution of an alkaline carbonate is poured, in the cold, upon pulverised arsenious acid, no effervescence is observable, but with the help of heat a slight effervescence is produced, which is owing to a disengagement of carbonic acid.

* The arsenites of alkalies appear to be the only salts of arsenious acid which are soluble in water. The combinations of

this acid with the earths and the metallic oxydes, seem to be insoluble, or nearly so. They have not, however, been well examined.

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[1] According to Guibourt, 100 parts of boiling water dissolve 9.68 parts of the vitreous acid, and 11·47 of the opaque acid, and when the solutions are cooled to 60°, 1·78 parts of the first and 2·90 of the second are retained in solution ; the first solution reddens litmus paper, but the second, far from reddening it, restores the blue colour of red litmus paper. According to Klaproth, 1000 parts of water at 60° dissolve from 2½ to 3 of opaque arsenious acid, and at 212° rather more than 77 parts, about 30 parts of which remain in solution after cooling.—ED.

[2] Brande mentions, that 80 parts of alcohol at 60° dissolve 1 part of arsenious acid, which is also soluble in ether and in fixed and volatile oils.—ED.

* The arsenite of lime, precipitated by a solution of chloride of calcium from one of arsenious acid to which ammonia has been added, is not insoluble in pure water[1].

* The aqueous solution of arsenious acid produces no precipitate in solutions of CHLORIDE OF BARIUM, CHLORIDE OF STRONTIUM, and CHLORIDE OF CALCIUM. But if the free acid be saturated with ammonia, an abundant white precipitate of arsenite of lime is immediately produced in the solution of chloride of calcium[2]. The solution of arsenious acid saturated by ammonia, does not form an immediate precipitate in one of chloride of barium, but after a pretty long time, a precipitate of arsenite of baryta is formed. The same effect is produced in a solution of chloride of strontium, but in this case, when the experiment is performed upon small quantities, the precipitate of arsenite of strontia appears only after several days, and is still less considerable than that produced in the solution of chloride of barium.

* BARYTA WATER becomes only slightly turbid when poured in excess in an aqueous solution of arsenious acid; when, on the contrary, an excess of LIME WATER is employed, an abundant white precipitate of arsenite of lime is formed, which is soluble in an excess of arsenious acid, and likewise in one of muriate of ammonia, and other salts of ammonia. The presence of free ammonia does not diminish its solubility in these re-agents. The precipitated arsenite of lime is but very sparingly soluble in solution of chloride of sodium, and still less so, though not quite insoluble, in a solution of nitrate of potash.

* Solutions of SALTS OF LEAD are not so delicate for precipi-

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[1] According to Berzelius, arsenite of baryta and of strontia are slightly soluble in water.—ED.

[2] Berzelius observes, that when the solution contains ammoniacal salts, especially muriate of ammonia, arsenite of lime is not precipitated; and, according to Gieseke, if solutions of ammoniacal salts, for example, of sulphate, nitrate, or muriate of ammonia, be added to the arsenite of lime already precipitated, it is re-dissolved; but the carbonate and the phosphate of ammonia decompose without dissolving it. In case of chemico-legal analysis, this observation is important.—ED.

tating arsenious acid as for precipitating arsenic acid, even when the two solutions have been saturated with an alkali. A solution of *acetate of lead* produces a precipitate in one of arsenious acid, saturated with ammonia only, when the latter solution is not too dilute. The arsenite of lead produced is decomposed by water, which takes up some of its arsenious acid. When precipitated by an excess of acetate of lead from a solution of arsenious acid, saturated with ammonia, the filtered liquid being rendered acid and then treated by a solution of sulphuretted hydrogen, gives a red precipitate, which, in point of colour, resembles sulphuret of antimony, but after removing the excess of the salt of lead by washing, a pure yellow precipitate of sesquisulphuret of arsenic always remains.

A solution of NITRATE OF SILVER determines no precipitate in an aqueous solution of arsenious acid, and only imparts an opaline yellowish-white tinge to the solution. But if the free acid be saturated by an extremely minute quantity of ammonia, the solution of nitrate of silver produces then a yellow precipitate of basic arsenite of silver, soluble both in dilute nitric acid and in ammonia. This precipitate is not insoluble in a solution of nitrate of ammonia, so that when a small portion of the yellow precipitate has been dissolved in a large quantity of nitric acid, it is not reproduced by carefully saturating the liquor with ammonia. This yellow precipitate has much resemblance with that produced by nitrate of silver in solutions of phosphates; yet its yellow colour is not so faint, and it is more soluble in acetic acid than the basic phosphate of silver.

* A solution of neutral SULPHATE OF COPPER renders an aqueous solution of arsenious acid scarcely turbid. But if the free acid be saturated by a feeble quantity of solution of pure potash, or of ammonia, a characteristic yellow-green precipitate of arsenite of copper (Scheele-green) is produced. This precipitate is soluble both in an excess of ammonia and of potash, and the solution in both cases has a blue colour. The green precipitate may be reproduced by saturating the blue solution in pure potash with muriatic acid, an excess of which re-dissolves it.

Both aqueous or gaseous SULPHURETTED HYDROGEN produces a yellow colour in the aqueous solution of arsenious acid, and after some time, or more rapidly with the help of heat, a yellow precipitate of sesquisulphuret of arsenic (sulpharsenious acid) is determined. But if a little muriatic acid be added to the solution of arsenious acid, that of sulphuretted hydrogen immediately produces the above yellow precipitate. This precipitate is very soluble in hydrosulphuret of ammonia, and likewise in a solution of pure potash, of ammonia, and even in a solution of carbonate of potash [1]. It has a deeper yellow colour than that produced by sulphuretted hydrogen in the acid solutions of the arseniates. It is also formed much more rapidly, even though there be only a minute trace of arsenious acid. When heated, it fuses and sublimes without alteration, if the experiment be performed out of the contact of the air. In order to distinguish these two sulphurets from each other, it is necessary, at the moment of their formation, to dissolve them in an excess of ammonia, and to add a solution of nitrate of silver to the liquor; sulphuret of silver is precipitated, which is to be separated by filtering, and the filtered liquid being exactly saturated with nitric acid, if a chocolate-brown precipitate of basic arseniate of silver is produced, it indicates that the sulphuret of arsenic produced by sulphuretted hydrogen, was a persulphuret of arsenic (sulpharsenic acid.) If, on the contrary, the precipitate by nitrate of silver is a pale-yellow basic arsenite of silver, the sulphuret produced by sulphuretted hydrogen was a sesquisulphuret of arsenic (sulpharsenious acid).

HYDROSULPHURET OF AMMONIA produces no precipitate in an aqueous solution of arsenious acid, but on adding a dilute acid to the liquor, a yellow precipitate of sesquisulphuret of arsenic (sulpharsenious acid) is produced.

* In qualitative analysis, the presence of arsenious acid in the arsenites, which are insoluble in water, is detected in the same manner as that of arsenic acid in the insoluble arseniates. The arsenite is to be dissolved in an acid, preferably in muriatic acid, and then, by means of sulphuretted hydrogen, arsenious

acid is precipitated from the solution; or else, if the oxyde with which the arsenious acid is combined, is also precipitable from acid solutions by sulphuretted hydrogen, the acid solution is to be saturated with ammonia, and then an excess of hydrosulphuret of ammonia is added, which dissolves the sesquisulphuret of arsenic produced, whilst the base remains in the state of metallic sulphuret. This liquor being now filtered, the arsenious acid may be precipitated in the state of sesquisulphuret of arsenic (sulpharsenious acid) by adding dilute muriatic acid. This method is preferred in the qualitative analysis of the green colours used by painters, and which consist essentially of arsenite of copper.

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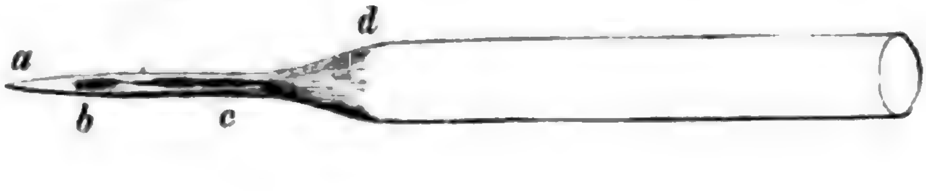
[1] This precipitate is also slightly soluble in pure water, to which it imparts a yellow colour, but if muriatic acid be present, it is not dissolved by this menstruum, and even water which contains some of it in solution, may be precipitated by adding muriatic acid, especially by boiling.—ED.

* Arsenious acid is, however, more easily detected in its compounds by means of the BLOW-PIPE than by qualitative analysis in the humid way. In order to detect the presence of arsenic acid in arseniates by means of the blow-pipe, the process is the same as for the arseniates. It is in such a case equally important never to omit to mix the compound with soda before exposing it upon charcoal to the internal flame, in order positively to ascertain the presence of arsenic by the alliaceous odour which is thereby developed. For the purpose of testing for pure arsenious acid with the blow-pipe, the operator must likewise begin by mixing it with soda and expose the mixture upon charcoal to the interior flame. The odour of garlic, which is developed whilst blowing, lasts pretty long. When the operator neglects to add soda, the arsenious acid is ordinarily volatilised with such a rapidity, that it often is not reduced, and the production of the characteristic odour fails.

* When the object is to demonstrate in an exact and indisputable manner the presence of the smallest quantities of arsenious acid, it is indispensable to proceed in the following manner:—A glass tube is to be drawn to a point until its diameter is about that of a strong knitting-pin, and the drawn out portion, which needs not be more than one inch in length, is closed at the flame of the lamp.

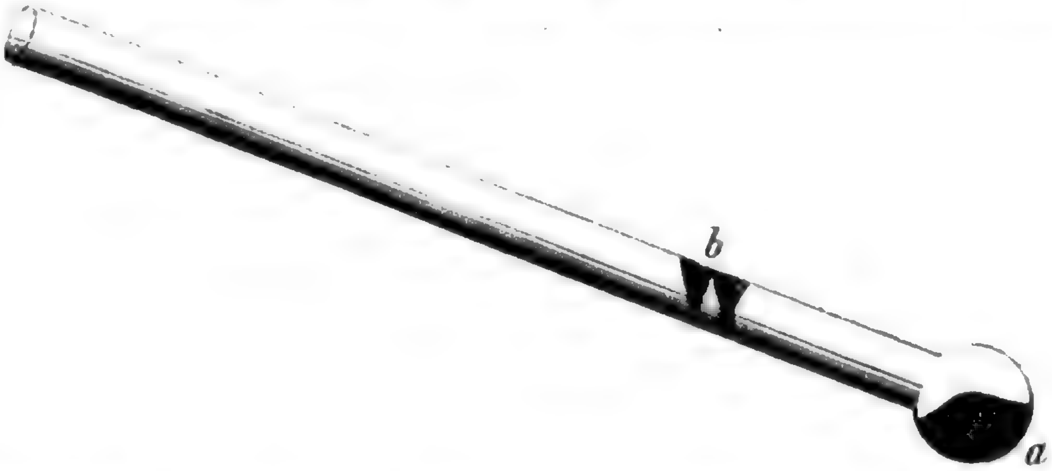


This done, the operator introduces in the closed end *a* the small quantity of arsenious acid under examination, and which may be less than 1 milligramme (0·0154 grain), and a whole piece of the charcoal used for blow-pipe experiments is slided down upon it, and must occupy the space between *b* and *c*. The tube is now to be carefully heated between *b* and *c* at the point where the charcoal lies, and when the charcoal is red hot, the point *a* is to be heated, so that the fumes of arsenious acid are obliged to pass upon the red-hot charcoal; the acid is thereby reduced, and produces in the colder part of the tube at *d* a black mirror of metallic arsenic. The best way of heating the tube consists in simply thrusting it in the flame of a spirit-lamp without using the blow-pipe. If the quantity of arsenious acid be very inconsiderable, a black coating only is obtained between *c* and *d*. But it is easy with the flame of the blow-pipe to drive the sublimate farther on, and to collect it there in the form of a narrow ring of metallic arsenic. The tube must now be cut at *c*, and heated for a moment at *d* in the flame of the spirit-lamp, in order to be convinced, by the odour of garlic which is then disengaged, that the mirror obtained was really produced by metallic arsenic.

* When, in the experiment just described, pulverised charcoal is employed instead of a whole fragment of charcoal, the air between the particles of the charcoal is dilated, and when heat is not carefully applied, some charcoal powder may pass in the larger part of the tube, which it blackens or soils; whilst by using a whole fragment of charcoal the experiment always succeeds, even when the quantity of arsenious acid is so small as to be imponderable with the most delicate scales.

* All arsenites appear to undergo decomposition by exposure to a red heat; yet the phenomena which are manifested during their ignition have not yet been studied with the care they deserve. Most arsenites, when heated, yield metallic arsenic and are converted into arseniates. When mingled with pulverised charcoal and ignited, those, the bases of which are very easily reducible, are converted into metallic arseniurets; such is the case, for example, with arsenite of copper (Scheele's

green), but with those, the bases of which are not reducible by charcoal, the arsenious acid only is reduced, and then it volatilises in the state of metallic arsenic; such is the case, for example, with arsenite of lime. In chemico-legal analyses often very minute traces only of arsenite of lime are obtained, and there is no better way to demonstrate the presence of arsenic therein than by means of pulverised charcoal. It is done as follows:—The arsenite of lime is to be dried, the quantity employed need not be greater than a few milligrammes[1], and then mingled with about three times its bulk of pulverised charcoal recently ignited; this done, the mixture is to be introduced in the little bulb *a*, blown at the extremity of a pretty strong small tube, and the interior of the tube is to be carefully cleaned with the feather of a quill in order to remove the charcoal dust which might have adhered. The bulb *a* is now to be heated at first very gently upon an argand spirit-lamp, taking care to incline the tube as shown in the figure, and the heat is gradually augmented until the bulb *a* becomes red hot; the reduced arsenic condenses in *b*. If the tube were less inclined, the water, which is always disengaged during the operation, would fall back in the red-hot bulb, and would break it; and if at the beginning the bulb was too strongly heated, the charcoal powder would be projected and would soil the tube. This last inconvenience may, however, be prevented as proposed by Stromeyer, by mingling the arsenite of lime with some oxalate of lime, which reduces arsenious acid as well as pulverised charcoal.



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[1] See at the end the corresponding English weights.—Ed.

* If to the mixture of arsenite of lime and charcoal a little boracic acid be added, the reduction is effected not only at a lower heat, but in a more complete manner still.

* When in chemico-legal analyses more considerable quantities of arsenite of lime are obtained, the reduction of the arsenious acid into metallic arsenic may be performed in a small retort.

* Sometimes it happens, in the course of a chemico-legal analysis, that arseniate of lime is obtained instead of the arsenite of that base, but the reduction into metallic arsenic is effected in the same manner, only the addition of boracic acid is more necessary in such a case than for the reduction of arsenite of lime.

* But in order thus to demonstrate the presence of the metallic arsenic contained in the arsenite or arseniate of lime, it is necessary that this salt be not mixed with too large a quantity of organic matter, because the empyreumatic oil produced during the ignition might conceal a small portion of arsenic, so much so that it might actually be difficult to perceive it.

* Arsenious acid and its compounds are so easily detected, especially with the blow-pipe, that their presence cannot be mistaken; it is with the arseniates only that the arsenites may be confounded, and in some cases it is very difficult to distinguish them from each other. The arsenites which are soluble in water, however, are identified by the colour of the precipitates formed by nitrate of silver and sulphate of copper in their solutions. They may also be recognised, but less readily, by the more or less deep colour of the precipitate produced by sulphuretted hydrogen in their acid solution, and likewise by the more or less prompt production of this precipitate. The soluble arsenites may also be distinguished from the soluble arseniates, because, when the solution of a salt of lime is poured in their solution, dissolving the precipitate thereby produced in a sufficient quantity of an acid of whatever kind, the addition of an excess of ammonia determines a precipitate which appears more speedily in solutions of arseniates than in those of arsenites.

* The salts of the two acids insoluble in water may be distinguished by dissolving them in muriatic acid, and precipitating by sulphuretted hydrogen. The sulphuret of arsenic thereby produced is examined, as has been said, page 342, in order to ascertain whether it corresponds to arsenic or to arsenious acid.

* The presence of ORGANIC SUBSTANCES, principally those which are not volatile, modifies the behaviour of arsenious acid and its compounds towards several re-agents : wherefore, when a chemist is legally requested to examine qualitatively organic substances which have been poisoned by arsenious acid, less importance must be attached to the phenomena produced by re-agents in such solutions, and which might lead to infer the presence of this acid, because several of these phenomena may be produced by organic substances alone.

* When a solution of arsenious acid in water contains certain non-volatile organic substances, for example, sugar, this foreign mixture does not hinder, but it retards the formation of the precipitate produced by an excess of lime water. The presence of other organic substances, *white wine*, for example, retards also the precipitation of arsenite of lime, which besides has, in such a case, quite a different appearance.

* When the solution of arsenites contains at the same time several non-volatile but uncoloured organic substances, the precipitate produced by nitrate of silver loses its yellow colour by long standing, and gradually becomes black. Nitrate of silver poured in a coloured solution ordinarily yields an immediate precipitate of a dingy colour.

* The yellowish-green precipitate, which a solution of *nitrate of copper* determines in the solutions of arsenites of alkalies, is not sensibly altered when the liquor contains non-volatile organic substances. It is also the case with the precipitate produced by *sulphuretted hydrogen* in the solutions of arsenites which have been acidulated with muriatic acid. When, however, the solutions are strongly coloured, the yellow colour of the precipitate produced by sulphuretted hydrogen is difficult to perceive.

* It is admitted that of all the re-agents which have been

enumerated, ***sulphuretted hydrogen*** is the most to be depended upon to recognise arsenious acid when the solutions are not too highly coloured. There are cases, however, in which this re-agent produces an abundant yellow precipitate in acid solutions which do not contain a trace of arsenious acid or even of metallic oxydes in general. Such is the case, for example, when very fat meat is boiled for a very long time with a solution of potash, supersaturating the alkaline liquor with muriatic or nitric acid and filtering. Also when such meat is boiled for a long time with either of these acids only, diluting the liquor with water, and filtering, by which last operation a clear liquid is often difficultly obtained. In either case sulphuretted hydrogen gas produces in such a filtered liquid an abundant yellow precipitate. The same effect is also produced when this solution, being saturated with an alkali, and hydrosulphuret of ammonia added, muriatic acid is further poured into it until it becomes acid.

* Still less than sulphuretted hydrogen can *sulphate of copper* be considered a certain re-agent to detect arsenious acid, because several slightly coloured decoctions of organic substances may thus produce a yellowish-green precipitate similar to that which arsenious acid forms with this re-agent, especially when a small quantity of potash is added. Thus, for instance, a decoction of unroasted coffee determines in solutions of a certain quantity of sulphate of copper, after addition of a little potash, a green precipitate, the hue of which resembles very much that of arsenite of copper; yet the supernatant liquor is also of a green colour and the precipitate itself dissolves in an excess of solution of potash, to which it imparts, *not a blue,* but a green colour. The green precipitate which a solution of sulphate of copper, with the addition of a little potash, produces in a decoction of onion resembles arsenite of copper still more. It is so much the more important to bear this in mind, that a solution of *nitrate of silver* determines also in a decoction of onion, with addition of a drop of ammonia, a yellow precipitate, soluble in dilute nitric acid and in ammonia, and which resembles arsenite of silver. Yet the hue of this precipitate is more dingy than that of arsenite

of silver, and it spontaneously turns black by long standing. A solution of unroasted coffee yields with nitrate of silver a white precipitate only, which the addition of a drop of ammonia immediately renders black.

* When the object in view is to know whether an organic substance contains arsenious acid, two methods may be resorted to for the purpose of separating this acid so as to be able to obtain metallic arsenic, and thus become utterly convinced of the presence of this metal.

* One of the methods consists in precipitating arsenious acid by means of *lime water* in the state of arsenite of lime; the other, by means of sulphuretted hydrogen, in the state of sulphuret of arsenic.

* When the organic substance, poisoned by arsenious acid, forms a turbid solution instead of a clear one; or when small quantities of arsenious acid are mixed with solid or pasty substances, it is first of all necessary to examine whether the sediment of the liquor or the solid or pasty substance contains any undissolved arsenious acid. From the sparing solubility of arsenious acid in water it generally occurs that in most cases of poisoning the acid has not been taken in complete solution, but in powder or in fragments mixed with the poisoned substance. In order to separate mechanically the undissolved arsenious acid, cold water is to be poured on the substance, and the mixture is to be well stirred. The arsenious acid frequently settles at the bottom with the other substances with which it is associated. If a grain, however small, of arsenious acid be thus obtained, it is easy to extract metallic arsenic therefrom by the means which have been previously indicated (page 344).

* If no parcel of solid acid be found, the whole mass must be submitted to chemical analysis. For this purpose a method is followed which my father was the first to propose. The solid organic substance is to be chopped into small pieces, for example, the whole of the stomach of the poisoned person, and it is boiled with its contents in a porcelain dish, with a sufficient quantity of water, to which from eight to fifteen grammes (120 to

245 grains) of pure potash have been added, according to the more or less considerable quantity of organic matter under examination. The pasty substances, such, for example, as have been ejected by vomiting, must be treated in the same manner. If no solid arsenious acid is found therein after boiling, the liquor must be passed through a piece of linen by pressing. The residuum may be treated a second time in the same manner, with half the quantity of water, and the two expressed liquids are mixed. By this process all the arsenious acid is dissolved, whether it was hidden in the folds of the stomach, or whether in extremely fine powder, because the potash added facilitates very much its solution. The potash dissolves at the same time a great portion of the organic substance, owing to which the liquor has a very dark colour. This expressed liquid is now to be heated, and nitric acid gradually added until the liquid has become acid, and of a golden-yellow colour. After complete cooling it is to be filtered, in order to remove the grease which has separated; carbonate of potash is then to be added to the solution, in sufficient quantity almost to saturate it, but not quite, and it is to be boiled for a few minutes, in order to expel the carbonic acid. An excess of lime water is now to be poured in the liquor, which is clear, and slightly acid, and before separating by filtration the precipitate which is thus produced, the whole must be boiled for some time. This precipitate, if arsenious acid be present, consists of arsenite of lime, ordinarily mixed with some phosphate of lime, and a very minute quantity of organic matter; sometimes also it contains arseniate of lime: it is collected on a filter, well washed, and carefully dried. When only a very small quantity is thus obtained, it should be ignited, as has been said (page 345), in order to extract metallic arsenic therefrom. If, however, the precipitate obtained is more copious, it is to be introduced into a small glass retort, to which a small receiver is connected, and gradually heated to redness upon charcoal; a coating of metallic arsenic is thus formed in the roof of the retort, or in the posterior part of its neck.

* This method always gives a certain result when the quantity

of arsenious acid contained in the poisoned substance is not too small; but it cannot be employed to detect very minute traces of arsenious acid, because arsenite of lime is soluble in a great number of salts, particularly in solution of chloride of sodium, and even in solution of nitrate of potash, of which latter substance the liquor under examination in the process, which has just been described, contains a large proportion. But as arsenite of lime is very soluble, more especially still in muriate of ammonia and other salts of ammonia, it is necessary to follow exactly the rules which have been exposed, and not to employ ammonia instead of carbonate of potash for the purpose of bringing the nitric acid liquor almost to a state of saturation; for, in such a case, no precipitate of arsenite of lime would be produced by addition of lime water.

* The second method for determining arsenious acid in *organic substances* consists in reducing it to the state of sulphuret of arsenic by means of sulphuretted hydrogen gas. If the liquor in which the presence of arsenious acid is suspected be perfectly clear, it may be easily rendered acid by adding a little muriatic acid, and a current of sulphuretted hydrogen gas is passed through it until complete saturation. It must then be left at rest in a cold or slightly warm place, in order that the sesquisulphuret of arsenic (sulpharsenious acid) may completely settle; when it has entirely lost the odour of sulphuretted hydrogen the sulphuret of arsenic is to be collected upon the smallest possible filter, and well washed.

* When the liquor which is suspected to contain arsenic is alkaline, hydrosulphuret of ammonia may be added, and the sulphuret of arsenic which has been thereby produced may be precipitated by muriatic acid. By this process, and by leaving the liquor at rest until it smells no longer of sulphuretted hydrogen, the arsenic is totally precipitated. This process should be adopted when the liquor contains arsenic acid instead of arsenious acid; for the former acid is more difficult to precipitate from an acid solution by sulphuretted hydrogen than arsenious acid.

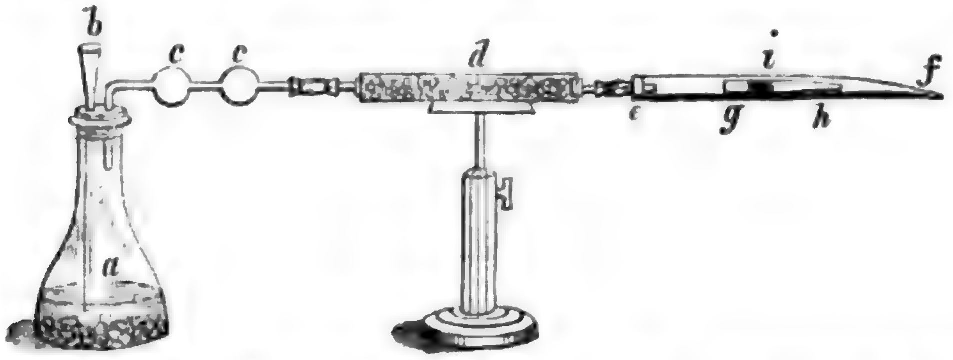
* But for greater security it is necessary to endeavour to

obtain arsenic in the metallic state from the sulphuret of arsenic; the operation is, however, attended with more difficulty than when we have to deal with arsenious acid and its combinations. If sesquisulphuret of arsenic (sulpharsenious acid) be treated upon charcoal before the blow-pipe, it is volatilised without emitting any odour of garlic; even when mingled with soda and the mixture is heated in the interior flame of the blow-pipe, the odour is not very sensibly developed. When sesquisulphuret of arsenic is heated before the blow-pipe in a somewhat long glass tube open at both ends, and held at a very acute angle, it is converted into sulphurous acid, which disengages, and into arsenious acid, which condenses under the form of a white sublimate in the upper and cold part of the tube. If the tube be less inclined it is converted into hyparsenious sulphuret, [protosulphuret of arsenic, or realgar, AsS,] which sublimes and condenses not far from the point exposed to the heat. In order to obtain metallic arsenic from a pretty large quantity of sesquisulphuret of arsenic, a portion thereof may be oxydised in a tube open at both ends, and the arsenious acid produced may then be reduced to the state of metallic arsenic. The process adopted to this effect is as follows:—The sesquisulphuret of arsenic is to be introduced into an open glass tube of the diameter of a quill, and four or five inches long; this tube is to be held as obliquely as possible, and heated before the blow-pipe precisely on the point occupied by the sulphuret, the vapours of which traverse the heated portion of the tube, and are oxydised; this roasting must be effected very slowly, in order that nothing should escape burning, and then, by means of the flame of the blow-pipe directed upon the arsenious acid which has deposited in the cold part of the tube, the whole may be collected to one point, immediately below which the tube may be drawn to a point, as has been said above, (page 344), into which drawn part of the tube the arsenious acid may be driven, and reduced by means of a fragment of charcoal. An unskilful hand very seldom succeeds in this experiment in conducting the roasting in a proper manner, but experience suggests the necessary precautions.

* When, in chemico-legal analysis, a very small quantity only of sesquisulphuret of arsenic has been obtained, the method which has just been described for obtaining metallic arsenic should not be resorted to, for fear it should not succeed. The best way, then, according to Berzelius, is as follows:—The sesquisulphuret of arsenic is to be collected on a very small filter, on which it is to be dried, and it is to be detached from the paper with all possible care. When the quantity of sesquisulphuret of arsenic obtained is so small that it cannot be separated from the filter, it is to be dissolved upon the paper itself by a few drops of ammonia, and the solution being evaporated at a gentle heat upon a watch-glass, the sulphuret may then be easily detached from the glass.

* This sulphuret is then to be mingled with an excess of soda, and kneaded into a paste with a little water, as is commonly done for tests with the blow-pipe. The moist mass is then introduced into a glass tube about one-sixth part of an inch in diameter, and one or two inches long; one end of this tube may be drawn into a point open at the end, but this drawn portion must not be too narrow. Ordinarily the moist mass is taken with a knife, and therewith introduced into the larger end of the tube. The small tube is then slid in the middle of another glass tube of a larger bore, and of a greater length, but likewise drawn at one end into a long point, open at the end. The whole is now united by means of a tube of caoutchouc to an apparatus for disengaging hydrogen gas, in such a manner that the portion of each tube which is drawn to a point, be placed opposite the phial from which the hydrogen is disengaging.

* In the following figure, *a* is a flask containing water and zinc, from which hydrogen gas is evolved by pouring sulphuric



acid through the funnel *b*; the gas evolved traverses first the bulbs *c c*, in which the greatest part of the water which it has mechanically carried with it is deposited; hence it passes into the glass tube *d*, united to the disengaging flask by a tube of caoutchouc, and which tube *d* is filled with fragments of fused chloride of calcium, for the purpose of completely desiccating the hydrogen gas. From this tube the gas passes into the tube *e f* connected with it, and in the middle of which the small tube *g h* is placed, which contains in *g* the mixture of sulphuret of arsenic and of carbonate of soda.

* When the whole apparatus is full of hydrogen gas, which must pass through it slowly, the tube is to be very gently heated at *g*, where the mixture is, in order to expel the water; if the extremity *h* of the small tube be drawn to too fine a point its opening will be obstructed by a drop of water, and in that case the current of hydrogen gas will pass only through the large tube, which difficulty may at once be removed by leaving this opening in *h* sufficiently large. As soon as the mixture is dry, it must be very rapidly heated with the flame of a spirit-lamp with circular wick. The hydrogen gas then reduces the arsenic contained in the sulpharsenite of soda, and metallic arsenic condenses in *i*. If it be heated too slowly, a small quantity of undecomposed sulpharsenious acid is sublimed at the same time. By this process the presence of metallic arsenic is actually demonstrated, even when the experiment is performed with the smallest possible quantity of sesquisulphuret of arsenic [Sulpharsenious acid]. It is absolutely indispensable to pass the hydrogen through fused chloride of calcium, for frequently, if the gas be damp, the reduction does not succeed in operating upon small quantities of sesquisulphuret of arsenic.

* Liebig has indicated a simpler, but less accurate method of obtaining metallic arsenic from very small quantities of sesquisulphuret of arsenic. It consists in drawing out a glass tube until it has obtained about the diameter represented in the figure.

* In the drawn out portion *b*, a small quantity of the dry sulphuret of arsenic about to be examined is introduced, upon which a layer of recently charred tartrate of lime is placed, but without mixing the two, but so as nearly to fill the drawn out portion *b*. This being done, the part which contains the carbonised tartrate of lime is to be heated very gently, and the best way of effecting this is to expose it to the low flame of a spirit-lamp with circular wick. The heat must be gradually increased, and when the carbonised tartrate of lime is red hot, the extremity *b* of the tube must be put in the flame. The fumes of sulpharsenious acid traversing then the red hot mixture of lime and charcoal, are decomposed, the sulphur combines with the lime, forming sulphuret of calcium, oxyde of carbon gas is disengaged, and metallic arsenic is deposited at *a*. But it often happens in this experiment, that the greatest portion of the sulpharsenious acid is sublimed without decomposition, when the carbonaceous mixture is not hot enough during the passage of the above fumes. Wherefore, when the operator has only a very small quantity of sulpharsenious acid to operate upon, Berzelius' method is preferable to that of Liebig, though it is more complicated.

* According to Simon, *pure lime* may also be employed for the purpose of converting very small quantities of sulpharsenious acid into metallic arsenic. A small quantity of that substance must be introduced into a tube about one-sixth of an inch in diameter and closed at one end, and upon it some lime which has been recently prepared by igniting hydrate of lime, is placed. The bulk of the lime must be four times that of the sulphuret. About one-fourth of an inch above the lime, and where the arsenic will be deposited, the tube must be slightly drawn out, in order to offer as little surface as possible to the metal. The operator then begins by heating the lime to redness, and next the sulphuret of arsenic, in order to cause its fumes to pass through the red-hot lime, and the metallic arsenic is deposited in the narrow part of the tube.

* In this method it is necessary carefully to prevent the fumes from expelling the lime, which always takes place when the latter substance is too much pressed upon the sulphuret. If this mode of operation is carried on upon larger quantities than five centigrammes (0·7615 gr.), a portion escapes without being decomposed, because more lime must in this case be employed, and it is then difficult to keep it at a red heat without bending the tube. The spirit-lamp with circular wick is best for heating the lime, and the operator must so manage the heat that the glass tube does not fuse.

* The decomposition of the sesquisulphuret of arsenic is effected quite as well as by the above processes, by mingling it in a dry state with *oxalate of lime* in a glass tube of a small bore, closed at one end, and bringing the mixture to a red heat by means of the spirit-lamp with circular wick. It is true, that sometimes a small portion of the sulphuret escapes, but the most part is decomposed, and metallic arsenic is deposited in the colder part of the tube. When the arsenious sulphuret is mingled with an excess of oxalate of lime and a little carbonate of ammonia, the reduction into metallic arsenic is more complete still. By this process there is no fear that by heating too rapidly, the mass should heave up,—a circumstance of frequent occurrence when carbonised tartrate of lime or pure lime is employed.

* The extraction of metallic arsenic from sesquisulphuret of arsenic acid may also be very successfully effected by the following method, proposed by Fischer:—The sulphuret is to be dissolved in an excess of ammonia, which leaves the sulphur with which it might be mixed undissolved. A solution of nitrate of silver is now to be added to the liquor until a black precipitate of sulphuret of silver is no longer produced; this precipitate is to be separated by filtering, and to the filtered liquid a little chloride of sodium is added for the purpose of converting the arsenite of silver into chloride of silver, after which, it is to be carefully evaporated to dryness. The dry mass consists of arsenite and nitrate of soda, chloride of silver,

and chloride of sodium, of which an excess has been employed; it is then to be mixed with charcoal-powder and the whole heated in a glass tube, as we have said (page 345), by which means a mirror of arsenic may be obtained. The precautions which must be observed in this operation consist, first, in dissolving the sulphuret of arsenic in a quantity of ammonia, which must be such that the arsenite, and subsequently the chloride of silver, must also dissolve completely in this re-agent; then to pour on the ammoniacal solution of the sulphuret only the necessary quantity of solution of nitrate of silver, because otherwise, if the dry mass contained too much nitrate of soda, it might afterwards detonate, when it is ultimately heated with the pulverised charcoal. The sesquisulphuret of arsenic precipitated from the solutions of arsenic acid by means of hydrosulphuret of ammonia, may be treated in the same way; arseniate of silver is formed in the ammoniacal solution, after the addition of the nitrate of silver. This method may especially be employed in those cases where the arsenious sulphuret collected upon a filter is so small that it cannot be satisfactorily detached. The filter is then digested in ammonia, and the ammoniacal liquor is treated as we have said.

* When arsenious acid has to be detected in an *organic substance* in the solid or in the pasty state, or in a liquor to which organic substances have imparted a very dark colour, the substance must be treated by potash, exactly as it must be done for the conversion of arsenious acid into arsenite of lime, as we have said (page 350). The alkaline liquor is then to be decolorised by nitric acid, filtered, and cooled, after which a current of sulphuretted hydrogen is passed through, and when saturated by it, the yellow precipitate, after long standing, is deposited.

* This yellow precipitate, obtained from organic liquors by sulphuretted hydrogen, may sometimes contain no sulphuret of arsenic (page 348); most generally, however, when obtained from an acid liquid which did really contain arsenious acid, and also a large quantity of organic substances, it is found to contain these

substances in even larger proportion than the arsenite of lime obtained by means of lime-water for a similar purpose (page 350). It is therefore impossible, in most cases, to extract metallic arsenic from this impure sulphuret of arsenic by means of the processes which have been mentioned; for as soon as it is heated, either alone or mingled with other substances, a great quantity of empyreumatic oil is disengaged, which covers the mirror of metallic arsenic, or of the sulphuret of arsenic.

* The best process in such case is the following:—After having completely dried the precipitated sesquisulphuret of arsenic, which contains much organic matter, it is to be reduced to powder, and mixed in a small porcelain crucible with an excess of carbonate of soda, and some nitrate of potash, and the whole is to be fused over the spirit-lamp with circular wick. The presence of the carbonate of soda permits the oxydisement of the sulphuret of arsenic to take place without violence or loss. The cooled mass is then to be dissolved in water and the solution rendered acid by muriatic acid, then treated by sulphuretted hydrogen; or else hydrosulphuret of ammonia is to be poured in, and after this it is to be rendered acid. In either case, a long time must be allowed for the sulphuret of arsenic to precipitate completely, because by oxydising with nitrate of potash, the arsenious has been converted into arsenic acid.

* The sesquisulphuret of arsenic obtained is then completely free from organic substances, and may be converted into metallic arsenic by one of the methods described.

* The two methods by which arsenious acid is detected in organic substances, namely, by lime-water and by sulphuretted hydrogen, may be very conveniently combined. The operator begins by treating the organic substance as has been described (page 350), and tries to detect the presence of arsenious acid in the state of arsenite of lime. When the lime-water fails in producing a precipitate, or has given one which, being treated as has been said (page 345), yields no metallic arsenic, the liquor which has been tested by lime-water must be rendered acid by muriatic acid; a current of sulphuretted

hydrogen is then passed through the liquor, which will have dissolved the traces of the arsenious acid which may be present; and a precipitate of sesquisulphuret of arsenic is obtained.

* It has been proposed to treat the organic substance poisoned by arsenious acid with *aqua regia* or *chlorine gas*, in order to obtain at once a liquor which should not be dark, and thus avoid the boiling with the solution of potash; but this method is not so secure, and by it the arsenious acid is also converted into arsenic acid.

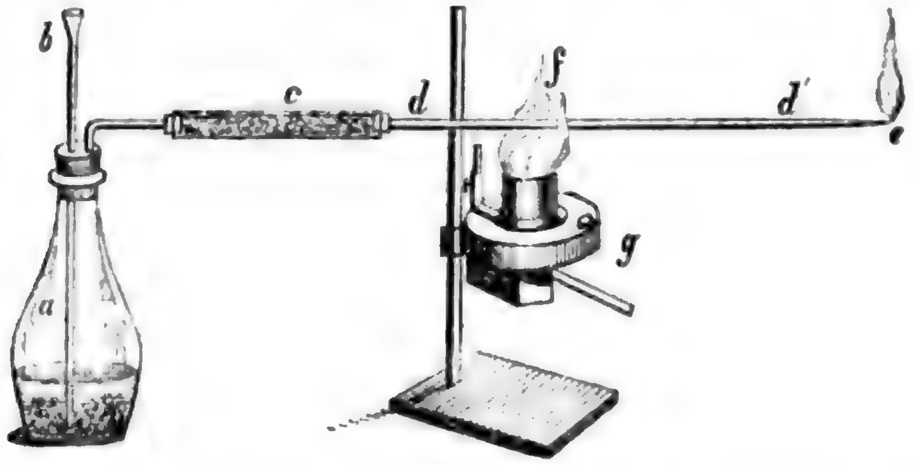
* The least available process is the treatment with *nitric acid*, because arsenious acid is too sparingly soluble in that acid.

* For the purpose of removing animal substances previous to precipitating the arsenious acid by means of sulphuretted hydrogen, Tauflieb uses a solution of *oxyde of zinc* in caustic potash, by which they are coagulated. Oxyde of zinc is separated in combination with the organic substances, and the arsenious acid remains dissolved in the potash. After filtering, the solution is rendered acid, and treated in the usual manner by sulphuretted hydrogen.

* But all the ordinary methods employed for extracting the metallic arsenic contained in liquids, either when in exceedingly small quantity, or when mixed with a great proportion of organic matter, are less to be trusted than that proposed by Marsh, and improved by Berzelius and Liebig, which consists in converting the arsenic into arseniuretted hydrogen, and in decomposing this gas by means of heat, which yields a deposit of metallic arsenic. The conversion of arsenic into arseniuretted hydrogen gas takes place by putting a little metallic zinc in the solution, and adding some dilute muriatic or sulphuric acid. The hydrogen gas which is then disengaged is passed through a glass tube heated red hot at one point by means of a spirit-lamp with circular wick. Not far from this point, arsenic condenses in the form of a brilliant metallic mirror, and when the quantity is very minute, or imponderable, it forms a brown spot.

* The best way of performing this experiment consists in taking an ordinary flask, such as is represented on the following page.

Zinc is put in the flask *a*, and a small quantity of the diluted acid is poured in through the funnel *b*. It is advisable to cause the hydrogen gas to pass through a small tube full of fused chloride of calcium *c*, and thence through a tube *dd′* of a very small bore. When the apparatus is completely filled with hydrogen, the gas may be kindled at the orifice of the small tube at *e*, and one part of it exposed at *f* to a red heat by means of the spirit-lamp with circular wick *g*[1]. This being done, the liquor which is suspected to contain arsenic is gradually poured through the funnel *b*; if this liquor be alkaline, it must first be rendered acid. When the liquor contains much organic matter, as when, for example, a stomach has been boiled in solution of potash, and the decoction has been rendered acid, not by nitric acid, but by muriatic or sulphuric acid, it is important to pour it in only by degrees, and by very small quantities at a time, because the disengagement of hydrogen gas produces a viscid froth which might ascend in the tube containing the chloride of calcium, especially if the flask be not very large. If the liquid really contains



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[1] It is necessary, before kindling the gas or putting the spirit-lamp under the tube, to wait until the disengagement of the hydrogen gas has proceeded for some considerable time, in order to make certain that all the atmospheric air has been expelled from the apparatus, else an explosion might take place. It is then *absolutely* requisite to ascertain that neither the zinc nor the acid employed contains arsenic. For that purpose, the gas being kindled and allowed to burn with a small flame, it is to be depressed by holding over it the bottom of a porcelain dish, and also by heating the central part of the tube by means of the spirit-lamp. If no black spot or incrustation appears either on the porcelain plate or in the tube, the acid and the zinc employed may be declared free from all trace of arsenic; and it is then and only then that the liquor to be tested may be introduced as described.—Ed.

arsenic, at first a brown spot is produced, and then a metallic mirror of arsenic not far from the portion of the tube which is heated by the spirit-lamp.

* Although the whole of the arsenic in a solution containing arsenious or arsenic acid will not have been disengaged in the state of arseniuretted hydrogen, owing to a portion being separated in the metallic state, which circumstance renders the method unavailable for quantitative analysis, it may, however, demonstrate in the most unequivocal manner the minutest traces of arsenic in liquids, for which testing by sulphuretted hydrogen presents difficulties. In effect, if the solutions are pure, limpid, and free from organic substances, Marsh's apparatus will indicate traces of arsenic so very minute, that the solution of sulphuretted hydrogen could not visibly precipitate them in the state of sulphuret.

* It is necessary that the sulphuric acid employed for disengaging the hydrogen be free from arsenious acid, which is readily ascertained when the gas which it disengages does not deposit arsenic whilst burning[1].

* It is also requisite that the zinc used in these investigations should not serve for subsequent researches of the same nature, because metallic arsenic might have precipitated at its surface, which would afterwards disengage arseniuretted hydrogen.

* Though this method is singularly ingenious and available, yet it has one feature which renders it uncertain. A liquor which contains antimony in the state of oxyde, disengages also, when treated by zinc in conjunction with an acid, hydrogen gas combined with antimony, which is decomposed by heat, and produces a mirror of antimony which has much analogy with the mirror of metallic arsenic. True, that when the quantity of antimony is very small, the stain is not brown, as occurs in such a case with arsenic; but this difference is not sufficiently characteristic. If the mirror of arsenic be heated in the tube in which it has formed, it volatilises; but this also takes place with the mirror of antimony, though for the latter

a stronger heat is required. There is scarcely any other means of distinguishing the two metals from each other in such cases, than to treat them by nitric acid or *aqua regia*, and to pass a current of sulphuretted hydrogen gas through the solution thus obtained, which in the first case precipitates the arsenious acid in the state of sesquisulphuret of arsenic; and in the second case, antimony in the state of sulphuret of antimony. But the experiment does not succeed upon very small quantities.

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[1] See the former note.—Ed.

To the French edition the following lines by E. Peligot are added:—

* "Since the publishing of this work, the researches on poisoning by arsenic have been the subject of numerous and important investigations. Soon after a trial, which has engaged public attention in the highest degree[1], several French chemists have most carefully investigated and discussed the relative advantages and defects of the various methods hitherto employed in chemico-legal analyses, and have been led either to propose new processes altogether, or else radically to modify the processes already known and in use for the detection of this dread substance."

* These labours, which have had the benefit of contradictory debates, were submitted to the judgment of the Royal Academy of Sciences of Paris; and a Committee, composed of Messrs. Thénard, Dumas, Boussingault, and Regnault, was intrusted with their examination. This Committee undertook also a long and elaborate series of experiments, with a view to solve the principal questions referring to the detection of arsenic in medico-legal researches; and the report which M. Regnault made in the name of the said Committee should be taken as a guide by those chemists who may be called upon to undertake the difficult task of investigating cases of poisoning by this substance.

* Although several of the processes recommended by the French chemists and the Committee of the Royal Institute have been already mentioned in the preceding pages, we have

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[1] That of Madame Laffarge.

thought it advisable to reproduce these processes in the present additional note, in order to preserve to the experiments the character of completeness, which, in our opinion, contributes to enhance their value and importance.

* In cases of poisoning by arsenious acid, the research of this substance may be divided into three principal operations:—

1. The concentration of the poisonous substance by means of the destruction of the animal substances with which it is associated.
2. The volatilisation of the poisonous body by means of Marsh's improved apparatus.
3. The examination of the volatilised product, and the demonstration of the principal characteristics of arsenic.

* Each of these operations being of paramount importance, requires the minutest care. If the product submitted to analytical research has not been properly prepared; if, for example, the suspected animal matter has not been entirely destroyed, the apparatus of Marsh, even though the said suspected animal matter should contain no arsenic, will show signs which may lead an inexperienced chemist into error; or if the said matter really contains arsenic, these signs will be so complicated as actually to render the presence of the poison doubtful.

* If, on the other hand, the substance under examination contains antimony, iron, mercury, these metals when treated by Marsh's apparatus will simulate the reaction of arsenic, which renders it absolutely necessary to submit the spots or rings or mirrors produced by the apparatus to an attentive examination, with a view to ascertain their true nature. The production of these spots or rings, which may likewise result from the imperfect combustion of the products under test, must be looked upon at most only as *probable signs* of the presence of arsenic, but are altogether insufficient, and cannot in any case whatever be received as positive proofs of the presence of arsenic.

* The process for the concentration of the poisonous substance must be such that the whole of this substance, even though the quantity contained in the animal matter be very

small, should as much as possible be preserved. "If," says the Report of the Academy of Sciences, "the analysist most generally can detect arsenic with facility in the poisoned food, or in the vomited matter, or lastly, in the excrement found in the intestines; cases occur in which all these substances are wanting, and in which the poison must be sought for in the body, in the tissues by which it has been absorbed. Such cases will present themselves, especially in corpses which have been buried, and which may have thus sojourned a certain lapse of time in the ground."

* M. Orfila has ascertained by numerous experiments that arsenious acid may be detected after death, in the blood, in the viscera, and in the urine.

* "In order to separate the arsenic which has been thus absorbed, the organic matter should be boiled for several hours in water, and yet this separation cannot be effected in a complete manner. The liquor thus obtained by boiling, contains a large proportion of organic matter in solution, and produces, with Marsh's apparatus, such a voluminous froth, that it is impossible to make use of it in a direct manner; it is absolutely necessary to destroy the organic matter in the solution, but in such a way as not to lose any of the arsenious acid.

"M. Orfila proposed two methods for effecting this.

* "The first consists in burning the organic matter by nitre, and consequently thus to convert the arsenic it may contain into arseniate of potash. The *modus operandi* is as follows:—

* "If the substance to be analysed be a liquid, urine for example, nitrate of potash is to be dissolved therein, and the whole evaporated to dryness, taking care to stir all the time, so as to obtain a homogeneous mass.

* "If the matter be pasty or solid, such as the liver, the spleen, muscular flesh, &c., it is to be cut and bruised in a porcelain or glass mortar, with about double its weight of nitre, the mixture being thus reduced into a thick paste, in which the nitrate of potash is evenly disseminated, and it is to be dried by a gentle heat in a porcelain capsula.

* "This operation being terminated, a new hessian crucible is to be brought to a dark-red heat, into which the organic matter, mingled with nitre, as above, must be introduced by small portions at a time.

* "If, as soon as the first portion thrown in the crucible has deflagrated, the product of the combustion, instead of being white or greyish, on the contrary remains black and carbonaceous, this colour indicates that the quantity of nitre employed is insufficient to effect the complete combustion of the animal matter, and therefore a fresh portion of nitre must be added in order to effect this perfect or complete combustion.

* "When all the mass has deflagrated, the product remains in the crucible in the fused state; the crucible is then to be withdrawn, and when it has cooled down, so that the substance therein has acquired a pasty consistence, a small quantity of distilled water is added in order to dilute the mass so as to pour it in a porcelain capsula. If a portion of the saline mass adheres to the crucible, it may be detached by boiling in it a small quantity of water, which is to be added to that in the porcelain capsula.

* "The saline mass is next to be decomposed by a slight excess of sulphuric acid added in small portions at a time, and the whole must be evaporated so as to expel entirely the nitrous and nitric acids, the presence of which would prevent the disengagement of hydrogen when treating the matter by Marsh's apparatus, and might even cause an explosion.

* "Lastly, the saline residuum being treated again by water, the solution thus obtained is introduced in Marsh's apparatus.

* "The second process indicated by M. Orfila, consists in treating the aqueous decoctions of the viscera by pure nitric acid, evaporating to dryness in order to char the animal matter, treating the charcoal by boiling water, and testing the liquor by Marsh's apparatus. The operator may also, and it is this last process which is preferred by Orfila, carbonise directly the organs under examination, by nitric acid. To effect this the viscera are first to be cut into small pieces, and dried, and then thrown

by small portions at a time into a porcelain capsula containing hot nitric acid. An abundant disengagement of nitrous acid fumes soon takes place, and shortly afterwards the fragments of organic matter are dissolved. When all the organic matter has thus been put in the capsula, the evaporation is to be continued until the thickened mass emits all of a sudden a thick smoke. The capsula must then be immediately removed from the fire, and the carbonisation is spontaneously completed. Should the capsula be suffered to remain longer on the fire, a very vivid deflagration would ordinarily take place, which would create a notable loss of arsenic. The charcoal thus obtained must be pulverised in a glass mortar, and boiled several times with distilled water, and the liquor is tested by Marsh's apparatus. When the charring has been carefully effected, the liquor is limpid and does not froth up, but if the carbonisation is not complete, if the charcoal resulting therefrom be greasy, the liquor obtained contains more or less organic matter, and when treated by Marsh's apparatus it froths up.

* "The charring by means of nitric acid is inconvenient, because to effect this, a large quantity of acid is required; but a drawback of a much more serious kind, and which it is often impossible to avoid even by the most careful watching, is the very vivid deflagration which may take place towards the end of the operation, and by which the greatest part of the arsenic may be volatalised[1]."

* A third method has been proposed by Messrs. Flandin and Danger; this method is as follows:—The portion of the viscus or of the flesh which is intended for examination, must be cut into small pieces, which are to be put in a porcelain capsula, and drenched with one-sixth, or a quarter of its weight of pure concentrated sulphuric acid. The proportion of sulphuric acid to be employed is dependent on the state of the animal matter; the fresher it is, the larger must be the proportion of sulphuric acid.

* The capsula being placed on the fire, the animal matter

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[1] Extracted from the Report of the Committee of the Royal Institute.

soon becomes liquefied and transformed into a black semi-fluid mass, which must be stirred all the while with a glass rod. When the matter has thus liquefied, and, in order to avoid projection, pieces of ignited charcoal are placed all round so as to heat the edges of the capsula, the treatment is to be continued until the matter has acquired sufficient consistence, so that all danger of intumescence or projection is over. The heat is then to be increased so as to heat the capsula in an equable manner until complete evaporation of the liquid.

* If the charcoal resulting from the operation is dry and brittle, it is a sign that the charring is as it should be, and that the quantity of sulphuric acid employed was sufficient. If, on the contrary, the charcoal obtained is greasy and cannot be readily pulverised, the capsula must be withdrawn from the fire, left to cool for some little time, drenched with a fresh portion of sulphuric acid, and heated again until vapours are no longer disengaged, and the charcoal has become dry and brittle.

* The capsula is now to be withdrawn from the fire and suffered to cool; the charcoal is next to be pulverised with a glass pestle and moistened with aqua regia, composed of three parts of nitric acid and one part of muriatic acid; both these acids must be pure and concentrated. By this addition of aqua regia, the arsenious is converted into arsenic acid, which is much more soluble. Heat is to be again applied, stirring all the while until the charcoal has become dry. In this state it is to be treated by boiling water, and the liquor, which is quite limpid and sometimes colourless, is introduced into Marsh's apparatus, in which it never produces any froth. "This process," continues the report of the Committee of the Academy of Sciences, "is much preferable to the carbonising by means of nitric acid; the operation is more easily controlled; a less quantity of the re-agents is required (which is a very important consideration), and deflagration never takes place. And we have acertained, by a great number of experiments, that by operating by this process upon two or three hundred grammes (about 30 or 40 thousand English grains) of muscular

flesh, to which only one milligramme (0·0154 gr.) of arsenious acid had been added, spots of arsenic were obtained, upon which all the characteristic reactions of arsenic could be demonstrated."

* This process, though simple and extremely delicate, rests however upon reactions, attended also with certain drawbacks which it is important to point out. If in effect the methods employed in chemico-legal analyses should be such as to leave no doubt as to the real nature of the poisonous substance separated, it is equally necessary that these methods, when in sufficiently skilful hands, should not cause the substances, for the separation of which they are employed, to be destroyed or dissipated. Now, the above process by sulphuric acid, as described, does not fulfil the latter condition, for it may cause the volatilisation and subsequently a loss of arsenic more or less considerable.

* The necessity in which the operator is placed of eliminating at the end of the operation the excess of sulphuric acid, requires a temperature sufficiently elevated, at least in some cases, to reduce the arsenious acid in contact with the charcoal produced by the animal matter, and to volatilise either the liberated arsenic, or else the undecomposed arsenious acid; the vapours of sulphuric acid must render this volatilisation still more easy.

* It does not seem possible so to manage the heat as completely to avoid all chance of loss, though this danger is much diminished when in the hands of chemists well versed in the manipulation of the process; but it must be admitted that, generally speaking, the necessity of obtaining a dry and brittle charcoal will lead, at least in some cases, to heating the mass to a temperature which may prove sufficiently high to volatilise all the arsenic. A process, therefore, which, in a theoretical point of view presents this inconvenience, furnishes results which are conclusive when positive, but doubtful or uncertain when negative.

* At any rate, this process requires to be modified, as was proposed by the Committee of the Royal Institute, by effecting the carbonisation not in an open capsula, but in a retort provided

with a receiver. The charcoal which is left in the retort must be well pulverised, and treated by a little nitric acid, dried again, treated by boiling water, and the liquid which may have distilled in the receiver is to be added thereto.

* And further, if the substance to be carbonised contains chlorides, it is to be feared that the arsenic may be carried away in the state of chloride of arsenic during the decomposition by sulphuric acid, or subsequently during the treatment of the charcoal by aqua regia; the arsenic, however, may be arrested whilst carbonising in a retort provided with a receiver, the inside of which must be previously moistened with water.

* Lastly, this process has another inconvenience, namely: as it is almost impossible that the sulphuric charcoal which remains after carbonisation should not contain sulphurous acid, the solution which contains it being introduced in Marsh's apparatus determinés the separation of the arsenic in the state of sulphuret of arsenic, and necessitates a modification of the processes employed for the identification of this body when obtained in the metallic state.

* To resume: the analyst has the choice between two methods of combustion; the one by sulphuric acid, the other by nitre. The latter, when well executed, appears preferable, the arsenic forming then a non-volatile combination (*arseniate of potash*); the danger of loss of this body must be less than that by the process of carbonisation by sulphuric acid. If, however, it be apprehended that some part of the mixture of nitre with the matter to be burnt, which mixture can never be perfectly intimate, if, we repeat it, there is reason to apprehend that this mixture should be acted upon by the heat before the reaction of the nitre takes place, which would cause a portion of the arsenic to disappear, this mixture may be further mingled with three or four times its weight of dry carbonate of soda, the object of this addition being to render the deflagration less rapid, and to produce the fusion and consequently the contact of the substances in the mixture before the combustion of the animal matter takes place. This process, it is true, has the drawback

of introducing in the analysis a somewhat large number of chemical re-agents, but this inconvenience disappears if the analyst takes care, as he always should before submitting the analysis to the last and definitive test in Marsh's apparatus, to make a blanc assay of all the substances which he employs.

* In effecting the combustion of the organic matter by means of nitre, as has been related above, but without addition of carbonate of soda, the Committee of the Academy of Medicine, who undertook also an important series of researches upon arsenic, in a medico-legal point of view, obtained, according to M. Caventou, who wrote the Report, results which were generally of a more clear and decisive kind than by the carbonisation by means of sulphuric acid.

* When the animal substances in which the presence of arsenic is suspected have been destroyed, the poison must be tested for by means of Marsh's improved apparatus.

* This apparatus, as first used and improved by Liebig and Berzelius, has been already described (page 359); therefore all that is necessary now is to point out here the further modifications which have been made to it.

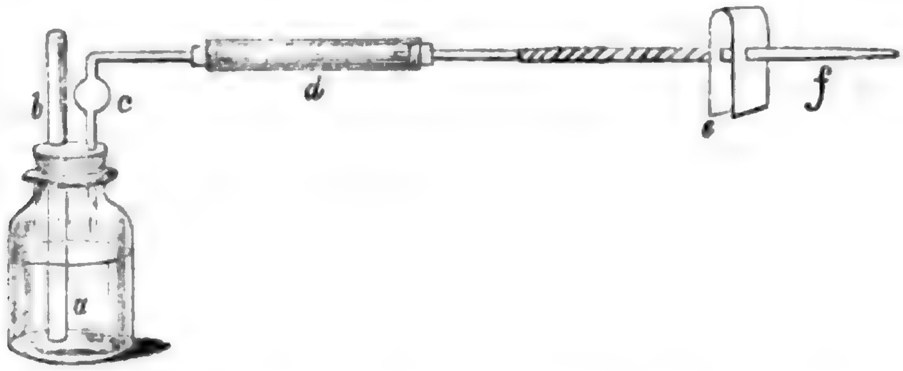
* It is known that when hydrogen gas is disengaged from a liquor which holds in solution an arsenical compound soluble in water, this gas is associated with a certain proportion of arseniuretted hydrogen gas, the presence of which may be immediately recognised by the following characters.

* 1st. Its being decomposed by heat. If the gas be passed through a glass tube heated to a dark red, the arseniuretted hydrogen is decomposed into hydrogen gas, which is disengaged, and metallic arsenic, which condenses under the form of a ring at a certain distance from the part of the tube which is exposed to the action of the heat.

* 2nd. Its incomplete combustion in the air. The jet of hydrogen gas mixed with arseniuretted hydrogen being kindled, the element more combustible than the other (namely, the hydrogen) burns first; so that if a cold substance (for example, a piece of china) be introduced into the flame, the arsenic

condenses upon it in the metallic state, forming shining spots of a dark-brown colour.

* By means of Marsh's apparatus these properties of arseniuretted hydrogen may be exhibited. The formation of the metallic ring must be preferred to the production of spots, for the greatest part of the volatilised arsenic may thus be assembled in one point, and quantities of arsenic which could not be perceived by means of spots, or if so in a doubtful manner, are rendered perfectly visible when tried for the production of the ring. Wherefore the Committee of the Institute has given the preference to an apparatus by which the arsenic may be isolated in the shape of a metallic ring. The disposition of this apparatus, which was indicated by Berzelius and Liebig, was further modified by Messrs. Kœppelin and Kampmann, of Colmar, as follows:—



* A flask with a large mouth *a*, is closed with a cork pierced by two holes. Through one of these holes a straight tube *b* is passed, plunging to the bottom of the flask; this tube is one centimetre in diameter: and in the other hole another tube of a smaller bore is placed, bent at right angles *c*, which is luted to another tube which is larger *d*, about three decimetres in length, and filled with asbestus. Another tube of German glass, being two or three millimetres in the bore, is adapted at the other end of the asbestus tube. This tube must always be several decimetres long, and drawn out at the extreme end *f*; one-third of which is to be wrapped in tinsel foil, as represented in the figure.

* The flask *a* must be chosen, so as to be able to hold all the liquid to be tested, and yet to leave about one-fifth of its total capacity empty. The comparative trials made by the Committee

of the Institute have proved, that in order to demonstrate the presence of very minute quantities of arsenic, it is advantageous to operate with Marsh's apparatus upon a liquid which will have been reduced by concentration to a small bulk.

* The extremity of the disengagement-tube *c*, which plunges in the flask, should be cut bevel, and have a bulb blown in the vertical portion. This disposition is not indispensable, but it is commodious, because it condenses almost all the water which is mechanically carried off, and which falls back in the flask: this water is in pretty considerable quantity when the liquid becomes hot from the reaction in the bottle.

* The apparatus being thus disposed, a few strips of zinc are introduced in the flask[1], and also some water, in order to close the opening of the safety-tube *b*, and then a little sulphuric acid is poured in. The hydrogen gas which is evolved, expels the air from the flask. The tube is to be heated red hot at the point wrapped in tinsel foil, by means of ignited charcoal placed upon a grate. A small screen prevents the tube from becoming hot at too great a distance from the part heated by the charcoal. The suspected liquid is next to be introduced through the open tube by means of a small funnel, in such a manner as to make it flow along the sides of the tube, in order to avoid sending air in the flask. If the disengagement of gas diminishes after the introduction of the liquid, a small portion of sulphuric acid is to be added, and the experiment is conducted slowly and as regularly as possible.

* If the gas contains arsenic, a metallic ring is produced at a short distance from the heated point in the tube. The operator may also inflame the gas as it issues from the apparatus, and try

to produce spots upon a china cup, for spots are sometimes obtained when a sufficient length of the tube has not been heated, or when its diameter is too large.

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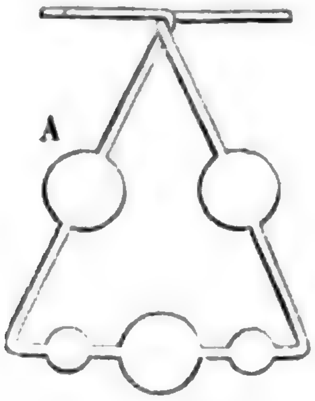
[1] The zinc employed must, of course, be free from arsenic. M. Meillet proposed the following method of preparing zinc free from arsenic:—A certain quantity of ordinary zinc is thrown, whilst in fusion, in a deep vessel full of water. The granulated zinc thus obtained must be reduced into smaller pieces in a mortar, and then placed in a hessian crucible in alternate layers, with one-fourth of its weight of saltpetre coarsely pulverised, taking care to begin by a layer of saltpetre and to finish by one of zinc; the crucible is then to be exposed to a good heat; a vivid deflagration soon takes place; when it is over the scories are removed, and the zinc is run into an ingot; it is then perfectly pure.—Ed.

* Before employing the process which has just been described, and which is a verbatim description of the Report of the Committee of the Institute, the method of concentration of the arsenical matter recommended by M. Lassaigne may be advantageously resorted to.

* This chemist proposed, instead of decomposing by heat, or of inflaming the gas which it disengaged from Marsh's apparatus, to pass the gas through a perfectly neutral solution of nitrate of silver. This solution is to be placed in a beaker, or better still, in a Liebig bulb-condensing-tube A. The arseniuretted hydrogen reacts upon the nitrate of silver, metallic silver is deposited, and the liquor contains arsenious acid in solution. The disengagement of hydrogen must be continued for a long time in order completely to absorb the arsenical compound with which it may be united. The excess of nitrate of silver in the solution may be destroyed by converting it into chloride of silver by means of muriatic acid. A liquor may be thus obtained by filtering or decanting, which, when evaporated, leaves arsenious acid, which may be easily recognised by the ordinary tests. The Committee of the Institute have ascertained that by this process the whole of the arsenic was retained; employed as a means of concentration, this process enables the operator to detect arsenic in liquors which contain such a small quantity of this poison, that Marsh's improved apparatus, as described before and employed directly, fails in showing its presence. But though



the solution of nitrate of silver may become turbid whilst being traversed by the current of gas, the operator must take care not to look upon this turbidness as a proof of the presence of arsenic; if, in effect, the zinc contains a little sulphur, or the sulphuric acid a little sulphurous acid, sulphuretted hydrogen will be evolved, and consequently a black sulphuret of silver formed in the solution of nitrate of silver. In some cases a deposit of metallic silver will be produced by carburetted gases, or even by pure hydrogen, if the apparatus be exposed to light during the operation. The presence of arsenic, therefore, must be considered as proved only when, the metal having been isolated in the liquor by Marsh's apparatus, as before described, the reactions which characterise that body shall have been produced.

* Lastly, M. Jacquelain has lately published a new process for extracting arsenic from a poisoned animal substance. Part of this method may be employed as a useful adjunct to the process adopted by the Committee of the Institute for isolating arsenic in the metallic form.

* M. Jacquelain places at the extremities of the tube in which the arseniuretted hydrogen is to be decomposed, a Liebig bulb-tube, as in the above figure, which is half filled with a solution of perchloride of gold for the purpose of washing the gas. The decomposing-tube is of German glass, about 4 decimetres long, and 3 millimetres in diameter, wrapped towards about the middle in tinsel foil, and there heated to redness by means of a spirit-lamp; the arsenic is deposited in the form of a metallic ring, but as a portion of the arseniuretted hydrogen always escapes being decomposed by the heat employed, this portion of the gas is decomposed by the perchloride of gold into arsenious acid, which is absorbed, whilst gold is precipitated in the metallic state.

* In order to recognise and determine quantitatively this arsenic, the gold of the perchloride in excess must be reduced by means of sulphurous acid, the excess of which gas being expelled by boiling, the liquor is to be filtered and distilled to

dryness in a retort furnished with a receiver, and a small quantity of the salt of gold which has not been reduced by the sulphurous acid is thus decomposed.

* The retort may then be washed with water acidulated by muriatic acid, and this liquor is to be added to the distilled product; the whole is then submitted to the action of a current of sulphuretted hydrogen. The excess of this gas being expelled by boiling, the liquid is to be decanted from the precipitate which will have formed, which precipitate being washed with hot water, is to be collected upon a small filter, and dried at 100° cent. (212° Fahr.) In this state the sulphuret is fit for the usual tests, that is to say, it may be converted successively into metallic arsenic, arsenious acid, and into arseniate of silver.

* It is evident that the reduction of the solution of gold, or of nitrate of silver, does not prove the existence of arsenic; for sulphurous acid, sulphuretted hydrogen and phosphuretted hydrogen (*phosphure trihydrique*), and other gases, can effect this reduction quite as easily as arseniuretted hydrogen.

* Having now related the various methods which may be resorted to, in order to concentrate and isolate the arsenic, there remains only to indicate the processes, by means of which the product obtained in the metallic state under the form of spots or of a ring is known to be really arsenic, and may be demonstrated and identified as such. We have seen that if the animal substances under examination contain an antimonial compound (tartar emetic, for example), they will, when treated by the method of concentration and insulation above described, produce reactions which may be confounded with those which belong to arsenic, from which they differ in a slight degree only. It is therefore indispensable, the arsenic being once obtained in the metallic state, to look for the physical and chemical properties which distinguish arsenic from antimony. Hence it will be necessary to ascertain:—

* 1st. Its volatility, by heating the metallic ring produced in the decomposition-tube, which metallic ring must be seen to shift

from place to place, under the influence of heat. It is known that in such circumstances antimony does not volatilise.

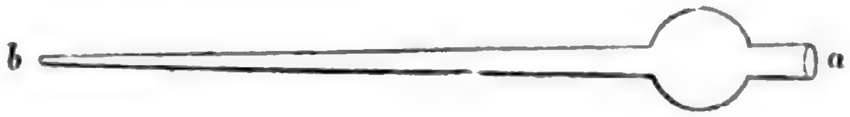
* 2nd. Its changing into a white volatile powder of arsenious acid by heating the tube open at both ends, and held in an inclined position.

* Antimony gives also a white powder, but this powder is much less volatile.

* 3rd. By heating a little nitric acid, or aqua regia, in the tube, the arsenic will be converted into arsenic acid, which is very soluble in water; the liquor being carefully evaporated to dryness in a porcelain capsula, will give a brick-red precipitate by pouring upon it a few drops of a perfectly neutral solution of nitrate of silver.

* Antimony treated in the same manner leaves a yellowish residuum insoluble in water, and which undergoes no change by contact with nitrate of silver.

* 4th. After these tests, the arsenic may again be reduced into the metallic state. To effect this, it is sufficient to add a little black flux[1] in the capsula, in which the precipitate by solution of nitrate of silver has been produced, to exsiccate the whole, and to introduce it into a small tube, one end of which is to be drawn out at *b*, and the other end *a* sealed up with the lamp after the introduction of the above mixture.



* The substance being introduced into the larger portion of the tube, it is to be heated to bright redness by the flame of the

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[1] Black flux is a mixture of carbonate of potash and charcoal, obtained by heating cream of tartar to redness in a closed crucible. Instead of black flux, as here recommended, Fresenius and Babo recommend twelve times the weight of a mixture of three parts of dry carbonate of potash, and one part of cyanide of potassium; because when black flux is employed for the reduction of sulphuret of arsenic, only one-half of the arsenic is reduced to the metallic state, the other half remaining combined with the soda, whilst with the mixture of carbonate of potash and cyanide of potassium, the whole of the arsenic is reduced.—Ed.

argand spirit-lamp; metallic arsenic then volatilises and condenses in the narrow drawn-out part of the tube into a ring, which has all the physical characters of arsenic: a very minute quantity of arsenic is sufficient for this reaction.

* To these characteristics we may add the alliaceous odour which arsenious acid, or rather metallic arsenic, evolves, when a few particles are thrown upon ignited charcoal: to this last test may be submitted the metallic ring obtained by the reduction of the arseniate of silver by means of black flux.

* By means of these processes the presence of arsenic can be accurately detected, even when this body exists in only very minute quantities, mixed with animal substances. Numerous experiments have proved that one millionth part of arsenious acid may thus be easily detected in a liquid by means of the spots produced by Marsh's apparatus; by the use of nitrate of silver, or of chloride of gold, as a means of concentration, and the production of the metallic ring, still smaller quantities of arsenic may be detected[1].—E. P.

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[1] There are still other methods which have been discovered since, and recommended as unequivocal tests of the presence of arsenic. In order to complete this lengthy chapter, we beg to reproduce them here.

Reinsch's Test. This is a process of reduction or precipitation of metallic arsenic from a liquid containing arsenious acid or arsenic acid by *metallic copper*. It is as follows:—Into the liquid suspected to contain arsenic, a pretty large proportion of muriatic acid is to be poured, and a bar of perfectly clear and bright copper introduced into the acid liquid, and boiled for eight or ten minutes, when the copper will be found covered with a coating of arsenic, which will give it the appearance of a bar of iron. This test is so delicate that $\frac{1}{200000}$ of arsenic gives a very distinct reaction in the course of a quarter of an hour. When the copper is abandoned for a few moments in the hot liquor, the arsenic becomes detached; and it may be recognised as such by the odour which the detached particles evolve when heated. If the coating of arsenic is too feeble, the copper blade is to be withdrawn and moistened with nitric acid, and when the bar of copper has reassumed its proper colour, it is to be washed, and the solution obtained is to be tested in a very small Marsh apparatus. Antimony is also precipitated by copper, but the coating produced is purplish, and the detached particles being heated, evolve no odour of garlic. Lead and tin are not precipitated. Bismuth forms distinct crystalline spangles. Silver and mercury are not thus precipitated from a liquor which is diluted beyond $\frac{1}{200000}$, and are besides very different from those produced by arsenic. This test properly managed is good, but it is not so delicate as that by Marsh's apparatus, for liquors in which this test fails in detecting arsenic, show distinct traces of it when submitted to Marsh's apparatus, and if the liquid contains

21. ACIDS OF CARBON.

1° CARBONIC ACID, CO_2.

(Acide Carbonique.)

In the pure state, carbonic acid is a colourless, inodorous, incombustible gas, which can neither support combustion nor

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nitrates of salts of mercury, and other metals, the reactions by Reinsch's Method become doubtful, or are altogether impeded.

A Committee of the Academy of Sciences of Berlin have contrived an improvement of Marsh's apparatus, which is exceedingly accurate and more delicate than any other. This modification, simplified by Dr. Ure, as published in the supplements to his Dictionary of Arts, Manufactures, and Mines, is as follows:—

"A is a narrow glass cylinder, open at top, about 10 inches high, and 1¼ or 1½ inch "diameter inside; B is a glass tube, about 1 inch diameter outside, drawn to a point "at bottom, and shut with a cork at top. Through the centre of this cork, the small "tube C passes down air-tight, and is furnished at top with a stop-cock, into which "the bent small tube of glass (without lead) E is cemented. The bent tube F "is joined to the end of E with a collar of caoutchouc, or a perforated cork, which "will be found more convenient."

"The manner of using this apparatus is as follows:—Introduce a few oblong slips "of zinc, free from arsenic, into B, and then insert its air-tight cork with the attached "tubes. Having opened the stop-cock, pour into A as much of the suspected liquid, "acidulated with dilute hydrochloric or "sulphuric acid (each pure), as will rise "to the top of the cork, after B is full, "and immediately shut the stop-cock. "The generated hydrogen will force "down the liquid out of the lower orifice "of B into A, and raise the level of it "above the cork. The extremity of the "tube F being dipped beneath the surface of a weak solution of nitrate of "silver, and a spirit flame being placed "a little to the left of the letter E, the stop-cock is then to be slightly "opened, so that the gas which now fills the tube B may escape so slowly "as to pass off in separate small bubbles through the silver solution. "By this means the whole of the arsenic contained in the arseniuretted "hydrogen will be deposited either in the metallic state upon the inside "of the tube E, or with the silver into the characteristic black powder. "The first charge of gas in B being expended, the stop-cock is to be shut, "till the liquid be again expelled from it by a fresh disengagement of "hydrogen. The ring of metallic arsenic deposited beyond E may be "chased onwards by placing a second flame under it, and thereby "formed into an oblong brilliant steel-like mirror. It is evident that by "the patient use of this apparatus the whole arsenic in any poisonous "liquid may be collected, weighed, and subjected to every kind of "chemical verification. If F be joined to E by means of a perforated cork, it may

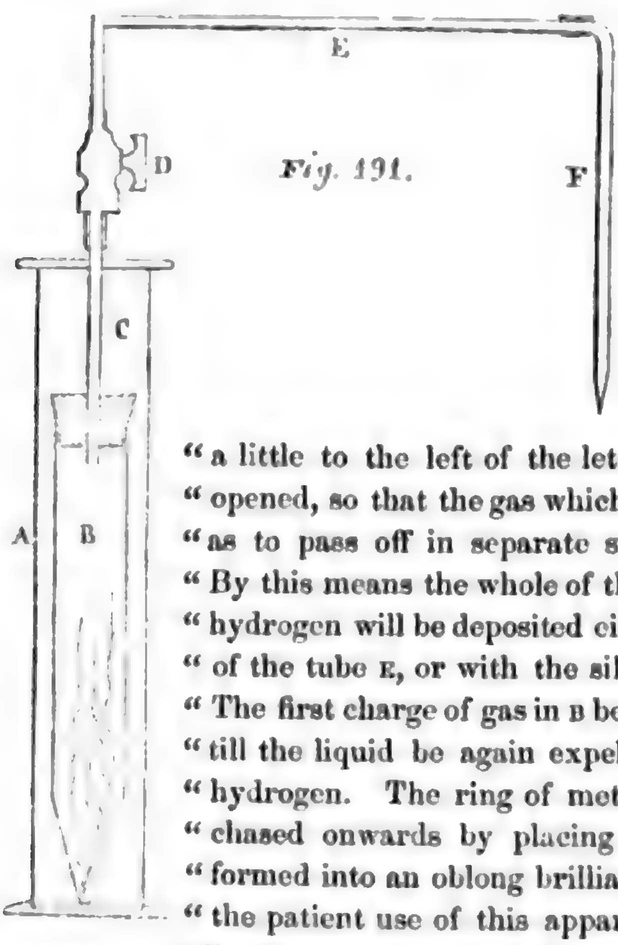
Fig. 191.

respiration. It is heavier than atmospheric air, owing to which it may be poured from one vessel into another, as if it were a

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" readily be turned about, and its taper point raised into a position such as when the " hydrogen issuing from it is kindled, the flame may be made to play upon a surface " of glass or porcelain, in order to produce the arsenical mirror."

" Or, the preceding process may be made supplementary to that of boiling the " arsenical foul liquor, acidulated with hydrochloric acid upon slips of clean copper, " whereby the arsenic is precipitated upon the copper in a metallic film or thin crust, " more or less brilliant. If one of the slips of copper thus coated be placed in the " tube B of the above-described apparatus, it will give off its arsenic without the " annoyance produced by the frothing up of a glutinous mixture."

Finally, Drs. Fresenius and Babo published in the *Annalen der Chemie und Pharmacie*, xlix., a method for the detection of arsenic in cases of medico-legal chemistry, which, according to Berzelius, seems to surpass all others in point of accuracy. It consists in extracting the arsenic from the organic substances by means of muriatic acid, and to convert it into arsenic acid, and by means of a solution of chlorate of potash, to precipitate the sulphuret of arsenic, which is then reduced by means of carbonate of soda and cyanide of potassium, heated in a current of dry carbonic acid. The modus operandi is as follows :—The operator begins by putting aside one-third part of the matter to be examined, as a *corps de reserve*, if need be ; that is, in case the first trial should fail. The two other thirds are to be mixed with a quantity of muriatic acid, about equal in weight to that of the dry substance under examination ; water is then to be added, so as to obtain a liquid paste. It is hardly necessary to say that the muriatic acid employed must not contain arsenic : this should of course be ascertained beforehand. The mixture is to be heated by means of the water-bath in a porcelain capsula, and when hot one half drachm of chlorate of potash, reduced to a fine powder, must be added every five minutes, until the mass becomes of a light yellow colour, and very fluid. Two drachms of chlorate of potash must now be added in one dose. After cooling, the whole is to be thrown upon a strainer of fine cambric, and the insoluble residuum is to be boiled with water so long as this fluid is acid ; the washings and the solutions must now be evaporated to about 1 lb., which is then to be mixed with a suitable quantity of water saturated with sulphurous acid, so that the liquor distinctly smells of it ; lastly, it is to be heated during about one hour, so as to expel the whole of the sulphurous acid.

The acid solution thus obtained has generally a dark colour ; it is to be saturated with sulphuretted hydrogen, and exposed for twelve hours to a temperature of 30° cent., until, in fact, the odour of sulphuretted hydrogen has vanished. The precipitate produced is to be collected on a filter, dried by the water-bath, and then drenched with fuming nitric acid, which is to be added drop by drop, and which is to be expelled by the heat of the water-bath. What remains after this treatment must further be moistened with concentrated sulphuric acid, and the mixture heated for three hours by means of the water-bath, and then at a temperature of 150° cent. by means of the oil-bath, so as to carbonise the mass and render it brittle. The residuum is now to be treated at the heat of the water-bath with 10 or 20 per cent. of water, filtered, and the insoluble portion washed until the water passes free from acid, the washings are then added to the solution, and a current of sulphuretted hydrogen is passed through until complete saturation ; the precipitate formed is collected on a filter, from which it is removed by dissolving it with caustic ammonia, and evaporated by the water-bath ; the residuum is dried at 100° cent., and weighed liquid; yet, like all other gases, it becomes pretty rapidly diffused with atmospheric air[1]. It reddens blue litmus paper

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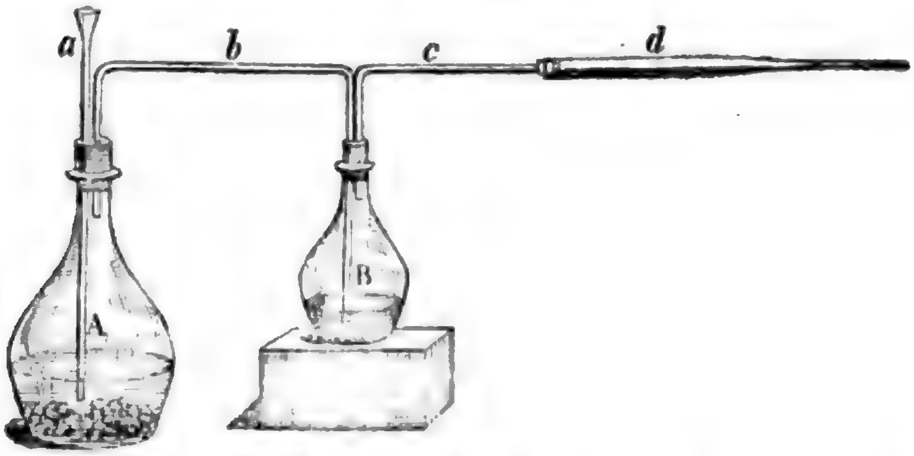
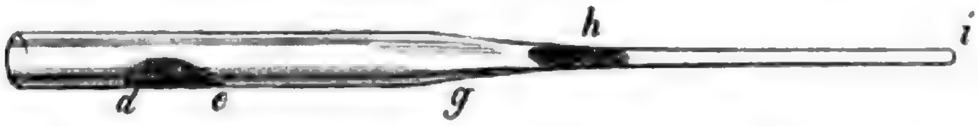
with the vessel in which it is contained. Part of this residuum is set aside as a reserve, and then the vessel is to be weighed, so that in deducting it from the whole weight, that of the sulphuret of arsenic may be known. The remainder of the process is conducted in the following apparatus:—



A is a large flask for disengaging carbonic acid; it is to be half filled with water, and some large fragments of limestone or marble (chalk does not yield a continuous current of carbonic acid). B is another flask of a smaller size, containing concentrated sulphuric acid. The larger flask A is closed by a cork, perforated with two holes, into one of which a funnel *a* is introduced, plunging nearly to the bottom of the flask, whilst from the other hole in the cork a tube emerges, through which the carbonic acid disengaged is led through concentrated sulphuric acid, which absorbs all its moisture. The gas thus dried escapes from the sulphuric acid flask through the tube *c*, into the reduction-tube *d*, an enlarged view of which is here given, on the scale of one-third of its real length:—



The apparatus being adjusted and ready, one part of the completely dry sulphuret of arsenic, or arsenite, under examination, must be triturated in a warm and polished mortar, for which purpose an agate mortar is best, with twelve parts of a mixture of three parts of anhydrous carbonate of soda and one part of cyanide of potassium, prepared according to Liebig's process (see infra). The pulverised mixture is now spread upon a piece of strong glazed paper, bent into a half cylinder or gutter, and introduced as far as *e* into the reduction-tube, when by turning the tube between the fingers half way round on its axis the powder on the paper falls down, of course, on the glass of the reduction-tube where it occupies the place marked between *e* and *d*; the card-paper is withdrawn, and by this means the rest of the tube is kept perfectly clean. This tube is now to be connected with the tube previously moistened with water, but the red colour which it has thus imparted to it disappears by exposure. Carbonic acid gas

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[1] On account of this rapid diffusibility of carbonic acid, the experiment of extinguishing a candle by placing it in a jar and pouring carbonic acid over it, succeeds only when the gas is poured from a wide-mouthed vessel (as, for example, from one beaker or jar into another jar); for if poured from a narrow vessel (for example, from a wine bottle) the experiment fails altogether.—Ed.

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c of the apparatus, and by pouring some muriatic acid in the funnel *a*, a stream of carbonic acid is disengaged at a moderate speed, which passing through the tube *b*, and thence through the sulphuric acid of flask B, escapes through the tube *c* into the reduction-tube *d*, and thence into the air. When after a little time the whole apparatus is completely filled with, and traversed by, the stream of carbonic acid, which must not be evolved at a more rapid rate than about one bubble per second of time, the tube containing the mixture *d e* must be gently heated through its whole length by means of a spirit-lamp, so as to dry it perfectly, as well as the mixture; after which the spirit-lamp is brought at the beginning or larger end of the reduction-tube, so as to make it red hot, and then a second and larger lamp is put under the mixture, so as to make that point red hot also, shifting it gradually and very slowly from *d* to *e*, and towards the drawn-out extremity of the reduction-tube, so as to completely reduce and volatilise the arsenic, and drive its fumes in that direction; and finally they are driven into the drawn-out portion, where they become condensed, as at *h*, into a metallic mirror, a minute portion escaping also at *e* into the air, to which it communicates the characteristic odour of garlic. When the volatilised arsenic has condensed as at *h*, the end *i* of the tube is fused, in order to close it, and heat being applied, the mirror of metallic arsenic may be shifted from place to place towards *h*, and back; in this manner the $\frac{1}{300}$th part of a grain of sulphuret of arsenic may furnish perfectly distinct metallic mirrors. Sulphuret of antimony, or any other compound of antimony, when thus treated, do not yield metallic mirrors. If there are other metals, such as lead, mercury, copper, tin, or antimony, they are found afterwards; the *lead* in the charcoal, after treatment by sulphuric acid; the *mercury* and the *copper* in the residuum left from the filtrate of the solution of the sulphuret of arsenic in ammonia; the *tin* and the *antimony* in the mass from which the arsenic has been sublimed.

Dr. Fresenius makes the following observations in his Instruction on Chemical Qualitative Analysis, a work most ably translated into English by Mr. J. Lloyd Bullock *. "If to arsenious acid (in the solid form, or in solution) some acetic acid be added, and subsequently an excess of potass, the mixture evaporated to dryness, and the residue finally ignited in a small tube, ALCARSIN (oxyde of cacodyl $C_4H_6As + O$) will be formed, which may be at once detected by its characteristic and insupportable odour. This odour changes immediately to the no less characteristic odour of chloride of cacodyl, when the ignited contents of the tube are mixed with a few drops of protochloride of tin, and are then exposed to the action of heat. This deportment of arsenious acid affords us likewise a means of determining whether metallic mirrors obtained by Marsh's apparatus are really arsenical mirrors or not. For this purpose, the metallic crust which it is intended to examine is boiled with water impregnated with atmospheric air until it is completely dissolved; the solution is mixed with acetic acid and an excess of potash; the mixture is evaporated to dryness, and the residue subsequently ignited in a small tube. In short, the whole process is conducted as I have just now described. BUNSEN has recently suggested this dissolves in water, but when the solution remains for a long time exposed to the air, or when it is boiled, the carbonic acid which it contains is almost entirely dissipated. The aqueous solution of carbonic acid reddens blue litmus paper precisely as the gaseous acid does, and the red colour likewise disappears by exposure. LIME-WATER, BARYTA-WATER, and STRONTIAN-WATER produce white precipitates of carbonate of lime, of baryta, or of strontia therein; but when only a small quantity of *lime-water* is poured in the solution, the precipitate disappears by stirring the liquor; and if even the quantity of *lime-water* added be more considerable, the precipitate produced dissolves upon adding a larger proportion of aqueous solution of carbonic acid[1].

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* Instruction on Chemical Analysis, by Dr. C. Remigius Fresenius, edited by J. Lloyd Bullock; second edition. John Churchill, Princes-street, Soho, 1846.

Of the salts which carbonic acid produces, those the base of which is an alkali are soluble in water, whether in the state of neutral or of acid carbonates. But the neutral compounds of carbonic acid with the earths and metallic oxydes, properly so called, are insoluble in water; wherefore the solutions of the earthy and of the metallic salts are precipitated by the solutions of carbonates of alkalies. When in these decompositions the carbonic acid does not combine with the base, it is then disen-

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method of testing arsenical crusts. It should be borne in mind, however, that these crusts dissolve but very slowly upon boiling with the aërated water."

From all that has been said, it appears that Dr. Fresenius and Babo's method of detection of arsenic is not so delicate as either Marsh's or Reinsch's tests, but that, on the other hand, it excels both these in certainty and accuracy, which is a consideration of the utmost importance in judicial investigation, in which a mistake on the part of the analyst may have the most fatal consequences. In the present state of science, the reduction of the sulphuret of arsenic by the mixture of carbonate of potash and cyanide of potassium should always be resorted to in preference to any other method.

Liebig prepares cyanide of potassium in the following manner:—8 parts of pulverised ferrocyanuret of potassium, previously rendered anhydrous by heating, are to be mixed with 3 parts of pure carbonate of potash well dried, and the mixture is put in a moderately hot iron crucible until the whole mass is in a state of tranquil fusion; the crucible is then withdrawn from the fire, and the fluid contents are poured upon a clean iron plate or on a slab of china, taking care not to permit any of the iron, which will have separated and which has subsided at the bottom of the crucible, to run with the fluid mass. When it has cooled it forms a milk-white mass, which, being broken, must be kept in a well-closed phial. It contains cyanate of potash in the proportion of 5 of cyanide of potassium and 1 of cyanate of potash, $5\ KCy + KO, CyO$.—ED.

[1] This is owing to lime being soluble in excess of carbonic acid.—ED.

gaged with effervescence, and the base separates; such is the case, for example, when the neutral salts of alumina are precipitated by carbonates of alkalies. Solutions of carbonates of alkalies are precipitated not only by the salts of the earths, but even by some of the earths themselves, such as by LIME-WATER, BARYTA-WATER, STRONTIAN-WATER.

* The carbonates of alkalies which contain an excess of acid are less soluble in water than the neutral corresponding salts. The solutions of some earthy or metallic salts are not precipitated by solutions of bicarbonates of alkalies, though the solution of neutral carbonates of alkalies may produce a precipitate in them. This is the case particularly with solutions of magnesia[1] (page 40).

The aqueous solutions of the carbonates are decomposed by all the acids which are soluble in water, and in the meantime carbonic acid is disengaged with effervescence. When, however, the quantity of the carbonate is very inconsiderable[2] no effervescence is produced, because the carbonic acid liberated remains dissolved in the water. When the carbonate exists in larger proportion, or even in very large proportion, the first drops of acid poured in the solution produce only a slight effervescence, which often is barely observable. This phenomenon is due to the liberated carbonic acid combining with the portion of the salt as yet undecomposed, and with which it forms a bicarbonate. It is therefore necessary gradually to add to the solution of the carbonate a sufficient quantity of acid to decompose it completely, when the carbonic acid will be disengaged with an effervescence, gradually augmenting also: when, on the contrary, a small quantity of the solution of the carbonate is poured in that of the acid, a strong effervescence is at once produced.

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[1] A neutral solution of a salt of magnesia is precipitated, for example, by solution of carbonate of potash, but not by one of bicarbonate of potash, because carbonate of magnesia is soluble in an excess of solution of carbonic acid, but if the solution be boiled, carbonic acid is disengaged, and a precipitate of basic carbonate of magnesia appears.—ED.

[2] Or, which is the same thing, in *very dilute solutions* of carbonates; carbonic acid being to a certain extent soluble in water, no effervescence takes place when treated by a free acid soluble in water. Hydrocyanic acid, however, and also hydrosulphuric acid (sulphuretted hydrogen) must be excepted, for the carbonates are not decomposed by these two acids. And in order to prevent mistaking air bubbles for carbonic acid, the substance supposed to be a carbonate should be first pulverised and treated with water, and well stirred; after which the acid may be added, which will disengage carbonic acid, if present. The gas disengaged may at once be identified as being carbonic acid, by connecting the vessel in which the experiment is performed with another vessel into which *lime-water* being poured, and agitated or shaken, an abundant precipitate of carbonate of lime will be formed.—ED.

All the carbonates which are insoluble in water being pulverised and treated by a free acid, are decomposed with disengagement of carbonic acid gas, and dissolve in the acid employed when their base is capable of forming a soluble compound with it. The consequence of this is, that after the carbonic acid has been completely disengaged, the insoluble carbonate can no longer be precipitated from the acid solution by an addition of ammonia, yet ammonia may produce a precipitate therein when the base of the salt is one of those whose salts, being soluble in water, are precipitable from such solutions by this re-agent; but in such a case the precipitate consists of the base only. This property distinguishes all the precipitates produced by the carbonates of alkalies from those produced by other salts of alkalies, the acids of which, like carbonic acid, form insoluble compounds with the earths and metallic oxydes. When a solution of carbonate of potash or of soda is poured in a solution of chloride of barium or of calcium, or in that of other soluble salts of baryta or of lime, if the precipitate which will have then formed be dissolved in muriatic acid it can no longer be reproduced by supersaturating the liquor with ammonia; but when, instead of a carbonate of alkali, a phosphate of alkali, for example, is employed, if the precipitate which will then have been produced be dissolved in muriatic acid, a precipitate of phosphate of baryta or of lime is reproduced upon supersaturating the acid solution of the precipitate by ammonia. The effervescence which accompanies the decomposition of the carbonates has not a very characteristic odour. When these salts are decomposed by diluted sulphuric acid, and a glass rod moistened with ammonia is held over the vessel, no white clouds are observable. Carbonic acid differs in this respect from the other gaseous acids which sulphuric acid disengages with effervescence from their compounds.

In certain cases some insoluble carbonates do not disengage carbonic acid when treated by muriatic or nitric acid. This is more particularly the case with the native compounds of carbonic acid, magnesia and lime (bitter spar—Dolomite) and of protoxyde of iron (spathose iron) which combinations do not at first effervesce in the slightest degree when muriatic acid is poured upon them, unless they be previously reduced into small bits; but when heated with the acid they are decomposed, and they likewise effervesce when they are submitted in the pulverised state to the action of that acid. Carbonate of baryta, especially that which is found in nature, is hardly attacked by common nitric acid, yet the acid is no sooner diluted with water, than the carbonate of baryta dissolves in it with effervescence.

Ignition does not expel the carbonic acid from the neutral carbonates which have a fixed alkali for base, and the acid carbonates of fixed alkalies by being ignited lose only the excess of carbonic acid, becoming thereby converted into neutral carbonates. Neither is carbonate of baryta or of strontia decomposed by ignition. Submitted to a very strong heat in a small platinum crucible, by means of a spirit-lamp with circular wick, carbonate of lime loses only a feeble portion of its carbonic acid, but when hydrate of lime is treated in this manner, or when steam of water is passed over carbonate of lime when at low red heat, the carbonic acid may be expelled entirely. The other carbonates abandon their carbonic acid when calcined, and the temperature need not be very high to effect this object. The acids, or oxydes which play the part of acids but which are insoluble in water, such as for example silicic acid, titanic acid, tantalic acid, peroxyde of tin, &c., and which consequently cannot, by reason of their insolubility, expel carbonic acid from the solutions of carbonates, do expel the carbonic acid from the carbonates of alkalies when fused with them.

When carbonates of alkalies are mixed with pulverised charcoal and strongly calcined, their carbonic acid is expelled, which is converted by the charcoal into carbonic oxyde which escapes in the state of a gas.

The neutral carbonates, which are soluble in water, impart a deep blue colour to reddened litmus paper. The solutions of acid carbonates produce the same effect but less powerfully.

* Carbonates in the solid state or in solution are most easily distinguished from other salts by the disengagement of inodorous carbonic acid gas, which they produce with effervescence when treated by soluble acids.

2°. OXALIC ACID, C_2O_3.

(*Acide Oxalique.*)

* OXALIC ACID forms crystals which, exposed to a warm atmosphere, lose part of their water of crystallisation and fall into a white powder[1]. It is soluble in water, and the crystals often produce a decrepitating noise whilst dissolving. It is soluble also in alcohol. The aqueous solution is strongly acid. When the crystallised acid is rapidly heated, part of it is volatilised without decomposition, and condenses into a crystalline sublimate, whilst another portion is decomposed and converted into carbonic acid, carbonic oxyde, and formic acid.

* Oxalic acid forms salts which are soluble in water only with the alkalies and a small number of metallic oxydes, such as, for example, peroxyde of tin, oxyde of chromium, alumina, peroxyde of iron, &c. The neutral oxalates of alkalies are more soluble than the acid oxalates. The combinations which oxalic acid forms with most of the earths and metallic oxydes are either quite insoluble or sparingly soluble, yet all of them are soluble in the strong acids, a large quantity of which must often be employed to effect their solution.

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[1] Crystallised oxalic acid contains 52 per cent. of water of crystallisation, 28 of which may be expelled in a direct manner, but the 14 others cannot be permanently eliminated, except by combining the acid with a metallic oxyde ; for example, with recently calcined and well pulverised protoxyde of lead. The effloresced acid contains 20 per cent. of water. The crystalline sublimate produced by exposure to a strong heat of about 300° contains no water of crystallisation, but it very soon absorbs moisture.—ED.

* *Oxalate of lime* is, of all these salts, the most insoluble in water, wherefore the slightest traces of oxalic acid may be detected in a neutral solution by pouring therein a small portion of a solution of CHLORIDE OF CALCIUM, or another neutral salt of lime; a white precipitate of *oxalate of lime* is thereby produced, which, when the quantity of oxalic acid is inconsiderable, requires a pretty long time, or else the help of heat, to settle. Although this precipitate is soluble in muriatic and in nitric acids, yet it is not soluble in small quantities of these acids, and it is less soluble still in oxalic acid (page 35), acetic acid, and other organic acids. Wherefore a solution of oxalic acid or of binoxalate of potash produce precipitates in solutions of the neutral salts of lime[1]. A precipitate is likewise produced immediately when LIME-WATER is poured in a solution of oxalic acid, to determine which it is not even necessary to employ an excess of the re-agent. But the most distinguishing character of the behaviour of oxalic acid towards lime is, that a white precipitate of oxalate of lime is produced in the solution of SULPHATE OF LIME (which latter salt is very sparingly soluble), not only by solutions of the neutral oxalates, but also by solutions of acid oxalates, and even by *oxalic acid;* the turbidness is not immediately perceptible, but after a few minutes it is quite distinct. This is the best and principal character by which oxalic acid can be distinguished from other acids which form with lime, salts which are sparingly soluble or insoluble, for there is no other known acid which can produce a precipitate, at least so rapidly, in solutions of sulphate of lime.

* Solution of PARATARTARIC ACID is the only substance which in similar circumstances can produce in solution of *sulphate of lime* a precipitate of paratartrate of lime; but in such cases the precipitate requires a longer time (a quarter of an hour) for its production, and it has a more crystalline appearance. The

precipitates of oxalate of lime are insoluble in solutions of *muriate of ammonia.*

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[1] Owing to the solubility of oxalate of lime in muriatic and in nitric acids, *ammonia* must always be added before precipitating by *chloride of calcium*, or by *nitrate of lime*, in order to saturate the nitric acid or the muriatic acid liberated, which otherwise would prevent the formation of the precipitate.—ED.

* A solution of ACETATE OF LEAD produces an immediate white and abundant precipitate of oxalate of lead, which is very sparingly soluble in free oxalic acid, but which is soluble in *nitric acid,* and insoluble in *ammonia.*

* A solution of NITRATE OF SILVER determines immediately an abundant white precipitate of oxalate of silver, which is not dissolved by free *oxalic acid.* This precipitate is even difficultly soluble in *nitric acid,* but it is more soluble in *ammonia.*

* Oxalic acid produces immediately in solution of SUBNITRATE OF MERCURY a precipitate of oxalate of mercury.

* The solutions of neutral oxalates of alkalies, as also those of the acid oxalates and of oxalic acid, determine in the neutral, or even in the acid solutions of a great number of other salts having an earth or a metallic oxyde for a base, precipitates which have been treated of in speaking of the behaviour of each base towards re-agents.

* The solution of oxalic acid, and the solutions of all the oxalates in a free acid, for example in muriatic acid, reduce a solution of PERCHLORIDE OF GOLD with which it is boiled, more easily than the organic acids. When the solution contains a large quantity of *perchloride of gold,* the carbonic acid gas produced by the decomposition of the oxalic acid is disengaged with effervescence during the ebullition (page 169).

* When oxalic acid is added to a solution of *peroxyde of iron,* and an excess of *ammonia* is added to the liquor, the whole of the peroxyde of iron is thrown down, as is always the case when ammonia is poured in solutions of persalts of iron, the acid of which, in the pure state, is volatile. But if instead of pure ammonia an excess of *carbonate of ammonia* or *of potash* be employed, the liquor remains clear and red, and it is only after a very long time that a precipitate is produced by the *carbonate of potash*; but the greatest portion of the peroxyde of iron remains dissolved. By boiling, the peroxyde of iron is precipitated better, but not completely. An excess of CARBONATE

OF SODA, poured in a solution which contains oxalic acid, does not at first precipitate the peroxyde of iron, but the liquor becomes sooner turbid with this re-agent than with carbonate of ammonia or of potash. The precipitate, however, in such cases, is not pure peroxyde of iron; it is more heavy, and has a more yellowish tint. By boiling, the peroxyde of iron is tolerably precipitated, but not completely.

* If a concentrated solution of oxalic acid be poured upon pulverised PEROXYDE OF MANGANESE, RED LEAD, and PEROXYDE OF LEAD (*suroxyde plombeux* or *suroxyde plombique*), carbonic acid gas is soon disengaged with effervescence. The same effect is produced by pouring solutions of acid oxalates upon the same peroxydes; but the solutions of neutral oxalates produce it only after having added some muriatic acid to the liquor.

* When crystallised oxalic acid or oxalates are mixed with concentrated SULPHURIC ACID, and the whole is exposed to a moderate heat, a rapid disengagement of carbonic acid and of carbonic oxyde takes place with effervescence; if oxalates be employed in this experiment, rather more sulphuric acid is to be employed than is sufficient to saturate the base[1]. If the experiment be performed in a glass tube closed at one end, the gas may be inflamed at the orifice of the tube, and will burn with a blue flame. If this gas thus evolved be collected over water in a tube closed at one end, and then agitated therein with a little solution of pure potash, about half the bulk is absorbed; the remainder consists of carbonic oxyde gas, which being set fire to burns with a blue flame, and more vividly than it would do previous to being separated from the carbonic acid in the manner just described. If instead of a *solution of potash* the gases evolved be agitated with *lime water*, this liquid is rendered very turbid. The liquid which is left after having heated oxalic acid or an oxalate with concentrated sulphuric acid is not coloured; if it have assumed a black or brown tinge, the operator may conclude that the oxalic acid or oxalate employed was not pure,

but contained some organic matter, which, when in large proportion, gives rise to a disengagement of sulphurous acid gas, the odour of which may be distinctly smelt if the mixture of oxalic acid, or of an oxalate with sulphuric acid, be heated for a long time; this reaction is in fact the best test of the purity of oxalic acid and of oxalates. When instead of using ordinary concentrated sulphuric acid, *fuming sulphuric acid* is employed, the disengagement of carbonic acid and carbonic oxyde gases takes place, even in the cold, provided the oxalate be dry, or the oxalic acid have lost part of its water of crystallisation by efflorescence.

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[1] This conversion of oxalic acid into carbonic acid and carbonic oxyde, is caused by the sulphuric acid absorbing from the oxalic acid its constitutional water.—ED.

* All the oxalates undergo decomposition in various ways by exposure to a red heat. The neutral oxalates of fixed alkalies, oxalate of baryta, strontia, and lime are converted into neutral carbonates, with disengagement of carbonic oxyde. If they be calcined in a small retort the gas which is disengaged burns with a blue flame when set fire to. The carbonate which is left as residuum should be white, but it always has a greyish colour, even when the oxalate operated upon is as pure as possible. This colour is produced either because it is impossible to obtain the oxalate in a perfectly pure state, or perhaps because the disengaged oxyde of carbon loses a portion of its carbon. When impure oxalates of alkalies,—for example, the sorrel-salt of commerce,—is ignited, the residuum is often black: if a very strong heat is used for calcining oxalate of lime, the carbonate of lime which remains abandons part of its carbonic acid.

* *Peroxalates of alkalies* are converted by ignition into neutral carbonates, whilst at the same time a gas is disengaged, which is a mixture of a large quantity of oxyde of carbon, and of a small proportion of carbonic acid.

* *Oxalate of ammonia* being exposed to heat yields water, ammonia, carbonate of ammonia, carbonic oxyde gas, cyanogen gas, a peculiar substance called oxamide, and which is volatile and sparingly soluble in water.

* The combinations of oxalic acid with the bases, which are not

susceptible of uniting with carbonic acid, or the carbonates which part very easily with their carbonic acid by ignition, undergo, when submitted to a red heat, a decomposition, the result of which is that the bases alone remain, whilst equal volumes of carbonic oxyde and of carbonic acid are evolved. Such is the case with *oxalate of magnesia*, of *alumina*, of *protoxyde of manganese*, of *oxyde of chromium*, of *oxyde of titanium*, &c.

* The combinations of oxalic acid with the metallic oxydes, which are reducible by carbonic oxyde, undergo, when calcined, a decomposition, the effect of which is to isolate the metal in the reguline state, and to disengage carbonic acid only; such is the case with *oxalate of protoxyde* and of *peroxyde of iron*, of *nickel*, of *cobalt*, of *protoxyde of copper*, &c., yet in most cases the decomposition is not complete.

* Oxalic acid and the oxalates in the solid form are so easily distinguished by their behaviour with sulphuric acid, and when dissolved, by their behaviour with solution of sulphate of lime[1] that they cannot be confounded with other substances.

3°. ORGANIC ACIDS WHICH CONTAIN NO NITROGEN.

* CARBON and oxygen, in combination with hydrogen, produce a numerous series of acids, which are ordinarily called *non-nitrogenised organic acids.* These acids form with the bases salts which especially differ from those produced by inorganic acids, because when heated in a small retort they yield the same products as those furnished by other organic substances which are free from nitrogen, and leave a residuum which contains free carbon, to which it owes its black colour.

* The number of these organic acids is rather considerable, and the properties of several of them are not perfectly known, because they have hitherto been produced or extracted from natural substances in too small proportion to allow of a complete investigation.

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[1] The precipitate thus formed being soluble in muriatic acid, and nearly insoluble in acetic and in oxalic acids, and being converted into carbonate of lime by ignition. The precipitation of the oxalic acid by salts of lime is much promoted by addition of ammonia.—ED.

* And as they all consist of the same constituent principles, but united in various proportions only, it is exceedingly difficult, and even in many cases it is altogether impossible, to distinguish them by means of re-agents, especially when the analyst can dispose of only small quantities, which is frequently the case. It is only by investigating their capacity of saturation, and by making a qualitative analysis of their elements that they can be distinguished from each other. We shall see at the end of the second volume how these researches must be conducted.

* Some of these acids, however, are more frequently met with than others in the course of chemical analysis, because, in a scientific or in a technical point of view, they have more importance. Some of them are found in commerce, others are produced in a great number of chemical operations, owing to which larger quantities are procurable, and thus can be submitted to qualitative analytical research.

* The behaviour of these latter only towards re-agents will be briefly indicated, as also the system which should be adopted for the purpose of distinguishing them from each other by means of re-agents. They may be divided into two classes: 1st. A. Those which cannot be volatilised by heat without undergoing decomposition. 2nd. B. Those which can be completely, or almost completely, volatilised without being decomposed.

A. NON-VOLATILE ORGANIC ACIDS.

* In the free state, combined with water only, they blacken very much when heated, and after ignition in a small glass tube closed at one end, they leave a considerable residuum of free carbon. Their salts blacken also considerably under the influence of heat; those which they form with the fixed alkalies, baryta, strontia, lime, are thereby converted into a mixture of carbonates and of charcoal.

* When to the aqueous solution of these non-volatile organic acids a solution of a PERSALT OF IRON is added, the peroxyde of iron cannot be precipitated by *ammonia*, or by other soluble bases, either in the pure state, or in that of carbonate; the solution

remains perfectly clear. A precipitate of *peroxyde of iron* is produced only when an insufficient quantity of non-volatile organic acid has been employed. The presence of non-volatile organic acids prevents also ALUMINA, and many metallic oxydes from being precipitated by the *alkalies;* only in such cases a quantity of organic acid is required larger than that which is sufficient to prevent the precipitation of *peroxyde of iron.* The presence of metallic oxydes, when their solutions contain non-volatile organic acids, cannot be recognised, except by *sulphuretted hydrogen,* or (after first saturating the liquid with ammonia) by *hydrosulphuret of ammonia.* In order to detect *alumina* in such cases, the solution must be evaporated to dryness, the residuum ignited in order to destroy the organic acid, and what is then left must be treated by muriatic acid. Alumina may then be detected in this solution by means of the ordinary re-agents.

* The *non-volatile organic acids* may be distinguished from those which are volatile by the peculiar behaviour of their solutions towards solution of YELLOW PRUSSIATE OF POTASH (*cyanure ferrosopotassique*) in presence of *peroxyde of iron.*

* When peroxyde of iron is dissolved in a volatile acid, either organic or inorganic, if a solution of FERROCYANURET OF POTASH be added to the liquid, a precipitate of prussian blue is formed, even though the solution of the persalt of iron has been rendered basic, by adding thereto a little ammonia, but not in sufficient quantity to produce a precipitate of hydrate of peroxyde of iron; if ammonia be added in sufficient quantity completely to precipitate the hydrate of peroxyde of iron, the further addition of *ferrocyanuret of potassium* causes a deep reddish-brown precipitate of a basic persalt of iron, which precipitate is invariably produced when prussian blue is treated by ammonia.

* If, on the contrary, a non-volatile organic acid, such as, for example, *tartaric, paratartaric, citric,* or *malic acids,* be poured in the solution of a persalt of iron, and then if a very small quantity of ammonia be added, so as only to render the solution of the persalt of iron slightly basic, the further addition of *ferrocyanuret of potassium* does not produce any precipitate of

prussian blue, and if a large excess of ammonia be added, nothing is precipitated, the solution remains clear; it is only when there is too small a proportion of non-volatile organic acid that a brown colour does appear; but even then no precipitate is produced. The precipitate of prussian blue takes place only when the liquor is rendered acid by the addition of an acid of whatever kind, even a volatile organic acid. The same phenomena are likewise produced when the non-volatile organic acids are combined with peroxyde of iron, so as to produce soluble basic salts; in such cases, the addition of *ferrocyanuret of potassium* to the solution produces no precipitate of prussian blue, except the combination be neutral or acid, in which case such a precipitate is formed.

* Those substances which are not acid, not volatile, and which are soluble, such as *sugar*, behave like the non-volatile organic acids.

* *Phosphoric* and *arsenic acids* react in the same manner when their combinations with peroxyde of iron are dissolved in ammonia; *ferrocyanuret of potassium* produces no change in such a liquor, and it is only after having supersaturated them with an acid that a precipitate of prussian blue can be obtained.

a. TARTARIC ACID, $C_4+H_2+O_5$.

(Acide Tartrique.)

* TARTARIC ACID, which contains water of crystallisation, forms large crystals, which are not altered by exposure to the air, and do not thus lose their water[1]. This acid is very soluble in water, and is likewise easily soluble in alcohol.

* Tartaric acid forms with the alkalies, salts, which in the neutral state are much more soluble in water than in the state of acid salts. The supertartrates are not rendered more soluble by the addition of a larger quantity of tartaric acid, nor does

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[1] Even a heat sufficient to decompose tartaric acid cannot deprive the crystals of their water. Anhydrous tartaric acid, as well as anhydrous oxalic or nitric acid, in a free state, is unknown. The crystals of tartaric acid, according to Berzelius, contain 11·85 per cent. of constitutional water, but contain no water of crystallisation.—ED.

acetic or any other organic acid augment their solubility, but they are dissolved by the strong inorganic acids, such as sulphuric acid, muriatic acid, nitric acid, and even by oxalic acid. The combinations of tartaric acid with the alkaline earths are insoluble, or sparingly soluble, but they are easily dissolved by an excess of tartaric acid. The case is the same with the compounds of tartaric acid with most metallic oxydes, with which, however, when they constitute a weak base, tartaric acid produces salts, which are very soluble and deliquescent.

* I have already indicated (pages 2 and 3) how tartaric acid behaves towards solutions of POTASH. The reaction is characteristic. But the solutions of *hydrate* or *of carbonate of potash* are of no avail for detecting small portions of tartaric acid, because a slight excess of these re-agents is sufficient to prevent the formation of the precipitate of bitartrate of potash. It is much better, therefore, to employ saturated solutions (in the cold) of chloride of potassium, of nitrate, or of neutral sulphate of potash, an excess of which does not prevent the formation of the precipitate of bitartrate of potash, provided always that the quantity of liquid be not so large as to form a liquor so diluted that this salt will dissolve therein.

* It has been observed, (page 3), that bitartrate of potash is soluble in solutions of the pure alkalies, and of the carbonates of alkalies, and also in the strong acids. A solution of bisulphate of potash, to which either a large, or a moderately large quantity of solution of tartaric acid is added, yields no deposit of bitartrate of potash, at least only an insignificant one is produced in certain cases, when a large proportion of tartaric acid is mixed with a very small one of bisulphate. On the contrary, the solution of *sulphate of potash* produces in that of the soluble neutral tartrate, a precipitate of bitartrate of potash, which, however, is redissolved by an excess of the re-agent[1].

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[1] Bitartrate of potash is much less soluble in water mixed with alcohol than in water alone, and its solubility is not increased by either tartaric or acetic acid; wherefore it is advisable to add alcohol to the solution, and to employ *acetate* of potash in preference to other salts of potash as a test for tartaric acid. Violent agitation

* A solution of CHLORIDE OF CALCIUM, or of another soluble salt of lime, produces no precipitate in one of tartaric acid, even after a long time; if, however, the acid has been saturated with a base, for example, with *ammonia*, an abundant white precipitate of tartrate of lime is formed. A solution of SULPHATE OF LIME does not trouble one of tartaric acid, even after a very long time. LIME WATER added to a small quantity of tartaric acid in such a proportion that it (the lime water) predominates so as to turn reddened litmus paper blue, yields, in the cold, an immediate precipitate of tartrate of lime completely soluble in a small quantity of a solution of sal-ammoniac, but not in pure ammonia. This phenomenon takes place even though the *lime water* be diluted with a quantity of water equal to its own volume.

* When a solution of tartaric acid is added to a solution of *chloride of calcium*, and a solution of *potash* is further added, the latter, provided the quantity employed be not considerable, produces a precipitate of tartrate of lime, at the ordinary temperature, but an excess of solution of potash completely re-dissolves the precipitate, and the liquor becomes clear again. If, however, it be heated then, it becomes very turbid, owing to a separation of tartrate of lime, which, if it be abundant, causes the liquor to stiffen into a jelly by ebullition. After cooling, the precipitate disappears completely, and the liquor appears again as limpid as before heat was applied. These phenomena may be reproduced with the same liquor as often as the operator may see fit.

* A solution of ACETATE OF LEAD produces immediately in one of tartaric acid an abundant precipitate of tartrate of lead, insoluble in even a large quantity of water, easily and completely soluble by addition of ammonia.

* A solution of tartaric acid poured in one of NITRATE OF SILVER, does not render it turbid except ammonia be added

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promotes the precipitation of the bitartrate of potash thus formed; and if the solution be neutral, it is best to add acetic acid and then acetate of potash and some alcohol.—ED.

in sufficient quantity to saturate the acid, in which case a white precipitate of tartrate of silver is produced, which is easily dissolved by an excess of ammonia. A solution of neutral TARTRATE OF POTASH produces immediately an abundant precipitate of tartrate of silver, which, by boiling, is completely reducible into metallic silver, an effect which is not so well perceived with the precipitate produced by *tartrate of ammonia.*

* A solution of tartaric acid produces an immediate white precipitate in solution of SUBNITRATE OF MERCURY, (*nitrate mercureux.*)

* Free tartaric acid does not reduce PERCHLORIDE OF GOLD, even by boiling. After a very long time has elapsed, only an insignificant quantity of gold is found to have separated with a yellow colour. If, however, an excess of solution of potash be added, the gold is at once precipitated under the form of a black powder in a state of great division.

* When concentrated SULPHURIC ACID is poured upon crystals of tartaric acid, or of a tartrate, they do not become coloured in the cold; but after a somewhat long time, the sulphuric acid dissolves the tartaric acid, and it remains colourless; but if heat be applied, it immediately turns brown, and ultimately becomes of a very deep black colour, sulphurous acid being at the same time disengaged. *Fuming sulphuric acid* dissolves likewise in the cold the crystals of tartaric acid, with which it is left in contact for a long time, with frequent stirring, and then, even after a very long time, it only turns slightly brownish; but if heat be applied, then it turns brown, though more slowly than happens with the non-fuming acid, sulphurous acid is disengaged, and it ultimately becomes black. When, instead of tartaric acid, crystals of tartrates are heated with fuming sulphuric acid, it does not turn brown, but remains colourless[1].

* When tartaric acid is heated, the first impression of heat converts it into a colourless liquid, which an increase of temperature turns brown, and which ultimately becomes carbonised,

whilst, at the same time, it exhales very pungent vapours. The odour of the vapours resembles that of burning sugar. The quantity of charcoal left is very small. Several tartrates which have metallic oxydes for a base, emit likewise when heated an odour of caramel (burnt sugar), but which is weaker than that produced by the pure acid. The tartrates of alkalies do not emit this odour perceptibly.

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[1] Boiling in nitric acid partly converts tartaric acid into oxalic and malic acids. —ED.

* The behaviour of tartaric acid with solutions of potash, even that of tartrate of potash with this re-agent, is so characteristic, that tartaric acid cannot be confounded with any other acid which has been hitherto treated of. The peculiar odour which it emits by exposure to destructive heat is likewise characteristic[1].

b. PARATARTARIC ACID, $C_4H_2+O_5$.

[RACEMIC ACID.]

(*Acide Paratartrique.*)

* In combination with water, paratartaric acid forms crystals which at a moderate heat, effervesce, lose half their water, and fall into a white powder. Left exposed to the air, at the ordinary temperature, these crystals undergo no change. Paratartaric acid is less soluble in water and in alcohol than tartaric acid.

* Like tartaric acid, paratartaric acid forms, with the alkalies, salts which are much more soluble in the state of neutral than in that of acid salts. The salts which it produces with the alkaline earths are insoluble or sparingly soluble, but they dissolve in an excess of acid.

* A solution of POTASH behaves towards paratartaric acid as towards tartaric acid. The precipitate of biparatartrate of potash is produced in the same circumstances as that of bitartrate, except that the former is more rapidly formed because much less soluble than bitartrate of potash. The best method of

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[1] Paratartaric (or racemic acid) is the only acid with which it may be easily confounded ; tartaric acid may, however, be readily distinguished by the behaviour of the precipitates produced by *lime-water* and *sulphate of lime.* See *Paratartaric Acid.*—Ed.

detecting small quantities of paratartaric acid, consists in taking saturated solutions (in the cold) of CHLORIDE OF POTASSIUM, or of NITRATE, or of neutral SULPHATE OF POTASH, an excess of which may even be added to a solution of the acid. The acid paratartrate of potash is, like the bitartrate, soluble in the pure alkalies and carbonates of alkalies, and likewise in nitric, muriatic, and sulphuric acids; wherefore a solution of *bisulphate of potash* does not produce any precipitate of superparatartrate of potash in a solution of paratartaric acid, whilst a precipitate is produced by that re-agent in a solution of a neutral paratartrate, when not added in too large a quantity.

* A solution of paratartaric acid forms almost immediately an abundant precipitate of paratartrate of lime in a concentrated solution of CHLORIDE OF CALCIUM; if the latter solution be too dilute, the precipitate is formed only after some time. Paratartaric acid does not produce immediately a precipitate in solution of SULPHATE OF LIME, but in the course of a quarter of an hour the liquor begins to appear turbid, and shortly after a precipitate of paratartrate of lime is formed. An excess of LIME-WATER poured in a solution of paratartaric acid, so that the liquor may have an alkaline reaction upon reddened litmus paper, produces immediately, in the cold, a precipitate of paratartrate of lime, which is almost insoluble in a solution of muriate of ammonia; at any rate, a considerable quantity of this solution is required to dissolve a portion of it.

If a solution of CHLORIDE OF CALCIUM, and then immediately afterwards one of POTASH, be added to a solution of paratartaric acid, a precipitate of *paratartrate of lime* is produced, partially but not totally soluble in a large excess of solution of potash. This reaction distinguishes paratartaric from tartaric acid.

* A solution of paratartaric acid immediately produces in one of ACETATE OF LEAD a thick white precipitate of paratartrate of lead, very soluble in *ammonia*.

* A solution of paratartaric acid does not produce an immediate precipitate in solution of NITRATE OF SILVER, but after some time paratartrate of silver separates under the form of an

abundant white precipitate, by saturating the free acid by ammonia. This precipitate is soluble in an excess of ammonia.

* Paratartaric acid determines in solution of SUBNITRATE OF MERCURY (*nitrate mercureux*) an immediate white precipitate of paratartrate of mercury.

* The behaviour of paratartaric acid towards PERCHLORIDE OF GOLD is the same as that of tartaric acid (page 396.)

* If concentrated SULPHURIC ACID be poured upon crystals of paratartaric acid or of a paratartrate, a little paratartaric acid is dissolved by it. In the cold, however, the solution remains colourless; but after a long space of time, or by heating the liquor, the *sulphuric acid* reacts upon it as upon tartaric acid (page 397.)

* FUMING SULPHURIC ACID does not render paratartaric acid brown, in the cold, even after a long time; or, at least, if a brownish tinge be thereby imparted, it is exceedingly slight; but if heat be applied, an odour of sulphurous acid becomes immediately perceptible, though the liquor remains perfectly colourless. This reaction is characteristic and distinguishes paratartaric from tartaric acid. The paratartrates behave in the same manner.

* When paratartaric acid is heated, its behaviour resembles much that of tartaric acid and of its salts. That is to say, paratartaric acid and several metallic paratartrates disengage the odour of burnt sugar like tartaric acid.

* Tartaric is of all acids that with which paratartaric acid might be more easily confounded, especially as regards its behaviour with solutions of *potash*; but paratartaric acid is distinguished principally from tartaric acid by the behaviour of the precipitate produced by *lime-water* towards *muriate of ammonia*, and also by its reaction with *sulphate of lime*[1]. It

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[1] That is to say, *tartrate of lime* is soluble both in muriate of ammonia and in tartaric acid, though it separates again from this solution in muriate of ammonia after a certain lapse of time. On the contrary, *paratartrate of lime* is insoluble both in muriate of ammonia and in tartaric acid.

Solution of sulphate of lime in solution of free *tartaric acid* produces no precipitate, and in solutions of *neutral tartrates*, after some time, a minute precipitate only. On has some resemblance with oxalic acid by its behaviour with solution of sulphate of lime, but it differs from it by the phenomena which are produced when submitted to the action of heat or of concentrated sulphuric acid. These two characteristic reactions render it easy to distinguish paratartrates from oxalates.

CITRIC ACID, $C_4 + H \ + O_4$.

(*Acide Citrique.*)

* Free *citric acid* may contain variable quantities of water, and then it assumes the form of large crystals, or of a non-crystalline mass[1]. When pure it is not altered by exposure, and does not deliquesce in the air. It is very soluble both in water and in alcohol.

* With the alkalies it forms soluble salts which an excess of acid does not render less soluble; with the alkaline earths and most metallic oxydes it produces salts, which are sparingly soluble or insoluble. Those which it forms with such of the metallic oxydes as are weak bases are very soluble.

* Solution of POTASH always produces soluble precipitates with solutions of citric acid, or of the soluble citrates[2].

* A solution of citric acid produces no precipitate in solution of CHLORIDE OF CALCIUM. By saturating the acid by ammonia, a precipitate of [neutral] citrate of lime is produced, provided the solutions are not too dilute. In more dilute solutions no precipitate is immediately formed in the cold, but in the course of a few hours a precipitate of citrate of lime is produced, which at first is inconsiderable, but which augments in course of time. Yet when, after having mixed the solutions in the cold,

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the contrary, solution of sulphate of lime produces in solutions of neutral *paratartrates* a precipitate of paratartrate of lime, and in solutions of *free paratartaric* acid a white precipitate is also produced, but only after the lapse of about a quarter of an hour.—ED.

[1] Citric acid always contains one equivalent of constitutional water, but the proportions of water of crystallisation vary according to circumstances.—ED.

[2] It is owing to this that citric acid, like tartaric acid, prevents the precipitation of peroxyde of iron, of protoxyde of manganese, alumina, &c., by alkalies, because soluble double salts are thus formed which are not decomposable by alkalies.—ED.

no precipitate is obtained, the whole of the [neutral] citrate of lime is suddenly precipitated by boiling the whole immediately[1]. LIME-WATER poured in a solution of citric acid in sufficient quantity to give an alkaline reaction to the liquor, that is, so that the liquor will render reddened litmus paper blue, produces in the cold a very spare precipitate only when the solutions are very concentrated, and provided a large excess of lime-water be used. Yet if the lime-water be boiled with the citric acid, the whole becomes very turbid, and a considerable precipitate of citrate of lime is formed. The greater part of it is re-dissolved by the liquor as it cools. It is necessary for the production of this phenomenon that there be a considerable excess of *lime-water;* in the contrary case, if no more lime-water is employed than is sufficient slightly to supersaturate the acid, although the reddened litmus paper turns very sensibly blue, a precipitate of citrate of lime cannot be obtained either in the cold or by boiling. If the excess of *lime-water* is a little more considerable, no turbidness is produced in the cold: ebullition determines a precipitate of citrate of lime which completely disappears on cooling. This precipitate reappears upon again causing the liquor to boil, and it again disappears on cooling: this phenomenon may be reproduced until a great portion of the lime contained in the lime-water is converted into carbonate of lime by the influence of the atmospheric air[2].

* When to a solution of *chloride of calcium* a solution of citric acid is first added, and then a solution of *potash,* a precipitate of citrate of lime is formed, which is not altered by ebullition.

* Citric acid immediately produces, in a solution of ACETATE OF LEAD, an abundant precipitate of citrate of lead, which is sparingly soluble in ammonia. This precipitate is more

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[1] The production of the precipitate of neutral citrate of lime by chloride of calcium takes place only in a solution of citrate of ammonia, of potash, or of soda, for free *citric acid* is not precipitable by *chloride of calcium,* as just said, and even in solution of *citrate of ammonia* no immediate precipitate is formed by that re-agent at the ordinary temperature, unless the solution be concentrated.—ED.

[2] This effect is due merely to citrate of lime being more soluble in cold than in hot water.—ED.

soluble in that alkali when a considerable excess of citric acid has been employed[1].

* A solution of NITRATE OF SILVER is not rendered turbid by citric acid: if the acid be saturated by ammonia a white precipitate of citrate of silver is formed, soluble in an excess of ammonia.

* Citric acid determines an immediate precipitate of citrate of suboxyde of mercury in a solution of SUBNITRATE OF MERCURY.

* Citric acid behaves with solution of PERCHLORIDE OF GOLD like tartaric acid (page 397).

* CONCENTRATED SULPHURIC ACID in the cold dissolves citric acid and the citrates without being coloured thereby, even after the lapse of a long time. By stirring the mixture the acid becomes frothy, on account of the gas which is disengaged. This gas on being ignited burns with a blue flame, like carbonic oxyde gas[2], but the sulphuric acid is not coloured thereby, and no odour of sulphurous acid is evolved. It is only by a prolonged ebullition that the acid becomes at first brown, then black, and then sulphurous acid is disengaged.

* FUMING SULPHURIC ACID dissolves citric acid in the cold, without becoming frothy or coloured; by applying heat a gas is disengaged, which likewise burns with a blue flame. After a prolonged ebullition the sulphuric acid turns black, and sulphurous acid is disengaged.

* When citric acid is heated it fuses into a colourless liquid, after which it turns first brown and then black, very pungent fumes being at the same time evolved, but which have not the odour of burnt sugar. The charcoal which is left behind is not so voluminous as that which is left by tartaric acid.

* Free citric acid is very easily recognized by its behaviour with LIME-WATER; its salts may also be readily distinguished by their reaction with CHLORIDE OF CALCIUM. By means of

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[1] Solution of *citrate of ammonia*, or an addition of citric acid to the excess of ammonia employed, as just said, easily dissolves this precipitate.—ED.

[2] The gas evolved, according to Dr. Fresenius, is a mixture of carbonic acid and of carbonic oxyde.—ED.

solution of potash it may be distinguished from tartaric and paratartaric acids[1].

d. MALIC ACID, $C_4H_2O_4$.

(*Acide Malique.*)

* MALIC ACID is difficult to obtain in the crystallised state; it is generally in the state of a granular crystalline mass. It deliquesces in the air, the moisture of which it absorbs, and is thereby converted into a syrupy liquid. It is very soluble in water and in alcohol.

* With the alkalies it forms very soluble salts, the solubility of which is not diminished by an excess of acid. Its combinations with most other bases are likewise soluble.

* A solution of POTASH always produces a soluble precipitate in solution of malic acid, or of the soluble malates.[2]

* A solution of CHLORIDE OF CALCIUM is not troubled by one of malic acid, even by saturating the acid with *ammonia*. If, however, ALCOHOL be added to the liquor, a white precipitate of malate of lime separates. Neither solution of SULPHATE OF LIME, nor even LIME-WATER in excess, can produce a precipitate in solution of malic acid[3].

* A solution of malic acid determines an immediate and abundant precipitate of malate of lead in solution of ACETATE OF LEAD. This precipitate, by boiling the liquor, becomes agglomerated and viscid, as does rosin when treated by boiling water. The precipitate is redissolved by a larger quantity of malic acid, but again reappears immediately by saturating the free acid with ammonia, an excess of which, however, completely re-dissolves it.

* A solution of NITRATE OF SILVER is not troubled by that of malic acid. By saturating the free acid with ammonia a white

precipitate of malate of silver is produced, which after some time, even in the cold, becomes blackish or grey. This precipitate is soluble in an excess of *ammonia*.

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[1] Tartrate and paratartrate of lead are very soluble in ammonia, whilst citrate of lead is only very sparingly so: this character may also serve therefore to distinguish citric from tartaric and paratartaric acids.—ED.

[2] Like tartaric and citric acids, malic acid prevents the precipitation of peroxyde of iron by alkalies.—ED.

[3] Of course the absence of those acids which produce with lime-water, chloride of calcium, and other salts of lime, precipitates which are sparingly soluble in water and insoluble in alcohol, should be first ascertained.—ED.

* The solution of malic acid at once determines a white precipitate of malate of suboxyde of mercury in solution of SUBNITRATE OF MERCURY.

* A solution of PERCHLORIDE OF GOLD behaves with malic acid in the same manner as towards tartaric acid (page 397).

* CONCENTRATED SULPHURIC ACID is not rendered brown by malic acid or the malates, but by protracted boiling it at first turns brown and then black, and an odour of sulphurous acid is evolved.

* FUMING SULPHURIC ACID dissolves malic acid and the malates in the cold, without becoming coloured. It is not coloured, either, by boiling, even after a long time: no sulphurous acid is evolved, and it remains colourless. This is a characteristic reaction which distinguishes malic from citric acid (page 403).

* When malic acid is subjected to heat it fuses, becomes coloured, and disengages pungent acid vapours which do not smell of burnt sugar[1].

* Malic acid differs more especially from the preceding organic acids by its behaviour towards LIME-WATER and CHLORIDE OF CALCIUM[2].

e. LACTIC ACID, $C_6H_5O_5$.

(Acide Lactique.)

* LACTIC ACID cannot be obtained in the crystallised state; when it has reached the highest point of concentration it forms a syrupy liquid, which is slightly soluble in water and in alcohol.

* With the bases it forms salts, most of which are soluble both in water and in alcohol. The lactates of alkalies crystallise with difficulty.

* The solutions of lactic acid and of lactates always produce soluble precipitates with solution of POTASH.

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[1] If the heat be raised to 392°, malic acid is resolved into *maleic acid* and *fumaric acid*, which reaction is quite characteristic. The *maleic acid* escapes with effervescence in the shape of pungent acid fumes: the residuum is *fumaric acid*. —ED.

[2] See the note, page 404.

* These solutions are not troubled by that of CHLORIDE OF CALCIUM and of other salts of lime, even when ammonia is added. LIME-WATER also fails in producing a precipitate when boiled with a solution of lactic acid.

* A solution of ACETATE OF LEAD does not trouble the solution of lactic acid, nor does it produce any precipitate in those of the lactates.

* A solution of NITRATE OF SILVER is not precipitated by one of lactic acid; yet, especially with the help of heat, it acquires a slight blackish tinge, which is due to a reduction of silver. Neither is a precipitate produced by saturating the free acid with ammonia.

* A solution of SUBNITRATE OF MERCURY determines immediately a white precipitate of lactate of mercury in that of lactic acid, provided the latter solution be not too dilute.

* A solution of PERCHLORIDE OF GOLD is not reduced by a solution of lactic acid, even by boiling the mixture. But if an excess of solution of POTASH be then added, reduced gold is precipitated after a long lapse of time, under the form of a black powder.

* A solution of neutral PERSALT OF IRON produces no visible precipitate in that of lactic acid, even by saturating the free acid with *ammonia,* or when the solution of a neutral *persalt of iron* is poured in that of a neutral lactate; neither does the liquor assume a blood-red colour, as is the case in similar circumstances with the solutions of acetates and of formiates. If after having poured lactic acid in a solution of *peroxyde of iron* an excess of *ammonia* be added, the peroxyde of iron is not at first precipitated by this last re-agent. In this respect lactic acid resembles the other non-volatile organic acids. Yet in order to prevent *ammonia* from precipitating a given quantity of peroxyde of iron, a much larger proportion of lactic acid is required than of tartaric, paratartaric, citric, or malic acids; and even though a very large excess of lactic acid may have been used, the liquor which during the first few days had remained perfectly clear begins, after a longer space of time (a few weeks),

to deposit peroxyde of iron. When in a solution of persalt of iron less lactic acid has been poured than is necessary to prevent the precipitation of peroxyde of iron by ammonia, and ammonia is then added, the liquor remains clear, and the excess of volatile alkali in the course of a few hours determines the separation of the peroxyde of iron. In this particular respect, therefore, lactic acid somewhat resembles the volatile organic acids.

* CONCENTRATED SULPHURIC ACID becomes very hot when mixed with concentrated lactic acid; it turns brown, then black, and disengages an inflammable gas. The FUMING SULPHURIC ACID becomes hotter still, and turns brown, whilst a combustible gas is likewise disengaged.

* When lactic acid is heated it fuses, and if the heat be increased, a great portion may be volatilised without decomposition. A considerable residuum of charcoal is left. The volatile acid produced by the action of a high temperature has a very analogous composition, because it contains one atom of water less than the lactic acid of the anhydrous lactates. The solution of this volatile acid does not prevent (like the other volatile acids) the precipitation of peroxyde of iron by ammonia. The peroxyde of iron is rapidly precipitated by ammonia from a solution which contains this volatile acid, and it soon settles. The lactates turn very black when heated.

* Malic acid is, of all acids, that which resembles lactic acid most. It differs, however, from it in an essential manner by its behaviour with ACETATE OF LEAD.

B. VOLATILE ORGANIC ACIDS.

* IN a free state, and combined with water only, those amongst the acids under present consideration, which are liquid at the ordinary temperature, are completely volatilisable without leaving much charcoal. Those which may be obtained in the solid state often leave, when treated out of the contact of the air, a very small quantity of charcoal, especially if they be not perfectly pure. The quantity of the charcoal thus left is, however, and

in all cases, very inferior to that which is produced by the action of heat upon the non-volatile organic acids.

* The salts which these acids produce with the fixed alkalies, such as baryta, strontia, and lime, are converted by heat into carbonates mixed with charcoal; if the heat be well managed the quantity of charcoal is very trifling.

* When a solution of PERSALT OF IRON is added to that of these acids, or of their soluble salts, the peroxyde of iron may be wholly precipitated by the addition of an excess of ammonia or of another soluble base. The same thing happens when instead of a solution of persalt of iron a solution of alumina or of other metallic oxydes is employed.

a. SUCCINIC ACID, $C_4H_2O_3$.

(Acide Succinique.)

* SUCCINIC ACID, when pure, may be obtained in the form of large crystals. It is sparingly soluble in cold water, but more soluble in hot water; the concentrated hot solution deposits on cooling a great portion of the acid, which crystallises. This acid is likewise soluble in *alcohol*, but almost insoluble in oil of turpentine[1]. When ignited it burns with a clear blue flame, which is not fuliginous.

* It forms soluble salts with most bases: those which it produces with such metallic oxydes as act as weak bases are sparingly soluble or insoluble. In this respect, therefore, its behaviour is the very reverse of the non-volatile organic acids.

* A solution of succinic acid produces no precipitate in solution of CHLORIDE OF CALCIUM even by saturating the free acid with *ammonia*. The other SALTS OF LIME OR LIME-WATER do not trouble this solution either[2].

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[1] According to Berzelius, 25 parts of cold and 1 of boiling water dissolve 1 of succinic acid. Cold alcohol dissolves it but with difficulty, whilst 1·5 of boiling alcohol dissolves 1 of succinic acid. Succinic acid is likewise soluble in ether.—ED.

[2] A mixture of alcohol, ammonia, and chloride of barium produces a white precipitate of succinate of baryta in solutions of free succinic acid and of succinates. This reaction is characteristic, and may serve to distinguish succinic from benzoic acid, as will be seen when this latter acid is treated of.—ED.

* A solution of ACETATE OF LEAD produces in that of succinic acid a precipitate of neutral succinate of lead, insoluble both in an excess of *acetate* of lead and of succinic acid[1].

* A solution of succinic acid determines no precipitate in one of NITRATE OF SILVER. After a certain time a little *succinate of silver* separates. When the free acid is saturated by ammonia a precipitate of succinate of silver is formed, which is easily dissolved by an excess of ammonia.

* A solution of SUBNITRATE OF MERCURY immediately produces a white precipitate of succinate of mercury in one of succinic acid.

* A solution of PERCHLORIDE OF GOLD is not reduced by one of succinic acid even with the help of heat. If an excess of solution of HYDRATE OF POTASH be added, no precipitate is produced, even by heating the liquor; it is only after a certain lapse of time that a black deposit of reduced gold is formed.

* A solution of neutral PERSALT OF IRON added to a solution of succinic acid produces, at least after some time, a voluminous precipitate of a cinnamon colour, which is persuccinate of iron, but the peroxyde of iron is not completely precipitated by free succinic acid. If, however, the acid be exactly saturated with ammonia, the precipitate obtained is more considerable, and the whole of the peroxyde of iron is precipitated in the state of persuccinate of iron, provided enough succinic acid be present. This precipitate is insoluble in water. When a neutral solution of a persalt of iron is mixed with that of a succinate, this precipitate is produced instanter. This precipitate is soluble in the free acids; an excess of ammonia renders it darker, less voluminous, and converts it into pure hydrate of peroxyde of iron[2].

* CONCENTRATED SULPHURIC ACID in the cold dissolves succinic

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[1] Dr. Fresenius says, that the precipitate of succinate of lead is soluble in an excess of succinic acid, of acetate of lead, in nitric acid, and also, but not so readily, in acetic acid.—ED.

[2] The succinic acid of the persuccinate of iron combines with the ammonia, with which it forms succinate of ammonia; generally, however, the precipitate is not a pure hydrate of iron, but a very basic succinate of the metal.—ED.

acid when pure, without being coloured thereby. If heat is applied it turns brown, and then black, but after a prolonged ebullition only, and sulphurous acid is disengaged.

* FUMING SULPHURIC ACID likewise dissolves pure succinic acid in the cold without being coloured thereby; after a prolonged ebullition it becomes brown, and then black, and sulphurous acid is disengaged.

* Succinic acid, even the purest, always leaves after ignition a charcoal[1], which is less in quantity than that resulting from all the other non-volatile organic acids submitted to the same treatment, but which is a little more considerable than that which results from the volatilisation of all the other volatile organic acids.

* Succinic acid may easily be distinguished from all the other acids hitherto treated of, by its volatility, and by its behaviour towards a solution of PERSALT OF IRON. If mixed with foreign substances these two characters may often appear less decisive, for in such cases the acid frequently leaves a rather large quantity of charcoal when heated, and the presence of foreign matter may often prevent the precipitation of the peroxyde of iron by ammonia. In such cases it is distinguished from tartaric, paratartaric, and citric acids by its behaviour towards CHLORIDE OF CALCIUM, and LIME-WATER; from malic acid, by its reaction with ACETATE OF LEAD, and by the properties of the malate of lead; lastly, from lactic acid, by its behaviour towards ACETATE OF LEAD and NITRATE OF SILVER.

b. BENZOIC ACID, $C_{14}H_5O_3$.

(Acide Benzoïque.)

* BENZOIC ACID forms crystalline spangles, or, if sublimed, needles of great brilliancy. In the purest state it is inodorous. When heated it fuses, and exhales fumes which strongly provoke

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[1] Berzelius and Dr. Fresenius say that *pure* succinic acid is volatilisable by heat without residue. All the succinates are decomposed by exposure to a red heat, except succinate of ammonia; the succinates of alkalies or of alkaline earths are thereby converted into carbonates.—ED.

coughing; if inflamed it burns with a very bright fuliginous flame. It is very sparingly soluble in cold water, but dissolves in very large proportion in hot water[1]. The hot solution loses on cooling the greatest portion of its acid, which crystallises. It is much more soluble in alcohol than in water, wherefore its alcoholic solution becomes turbid or milky when water is added thereto. It is largely soluble in oil of turpentine, especially with the help of heat; but this solution likewise abandons a great portion of the acid in cooling[2].

* Benzoic acid forms soluble salts with most of the powerful bases, almost all of which salts are more soluble in water than the free acids; wherefore, when a strong acid, capable of combination with the base of the salt, is added to the solution of a benzoate, the greatest part of the benzoic acid is precipitated under the form of a white powder, which at first renders the liquor milky. This phenomenon is quite a distinctive character for benzoates. With the weak bases the acid forms salts, which are sparingly soluble or insoluble in water.

* A solution of benzoic acid, saturated in the cold, produces no precipitate in a solution of ACETATE OF LEAD; but it produces a precipitate, though an inconsiderable one, of benzoate of lead when the acid is saturated with ammonia. This precipitate is not soluble in an excess of ammonia.

* A solution of NITRATE OF SILVER produces no precipitate in one of benzoic acid. If, however, the acid be saturated with *ammonia* a crystalline precipitate of benzoate of silver is formed, which is very soluble in an excess of ammonia.

* A solution of PERCHLORIDE OF GOLD behaves towards solutions of benzoic acid as towards one of succinic acid.

* A solution of neutral PERSALT OF IRON produces in solution of benzoic acid a voluminous precipitate of a brownish-yellow colour, of perbenzoate of iron. If the free acid be exactly saturated with *ammonia*, the whole of the peroxyde of iron is separated in the state of pure benzoate, provided there be a sufficiency of

benzoic acid; this precipitate is more bulky still than that of persuccinate of iron. When the neutral solution of benzoate of alkali and that of a persalt of iron are mixed together, the precipitate is at once produced. The free acids destroy it instanter, and dissolve it; but the benzoic acid is at the same time deposited in the form of a white powder, an effect which does not take place when the quantity of the precipitate is inconsiderable and that of the liquid in which it is produced too large, in which case the free benzoic acid liberated remains dissolved. An excess of ammonia converts the perbenzoate of iron into pure hydrate of peroxyde of iron, imparting a deeper tinge, and rendering it at the same time less bulky.

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[1] 200 parts of cold water at 60° are required to dissolve 1 of benzoic acid.—ED.

[2] Benzoic acid is likewise soluble in ether and in the fixed oils.—ED.

* CONCENTRATED SULPHURIC ACID does not turn brown by being poured upon pure benzoic acid in the cold, and if even heat be applied it does not become discoloured, nor is sulphurous acid evolved.

FUMING SULPHURIC ACID behaves in the same manner; but if the benzoic acid is not pure, it is rendered brown by concentrated sulphuric acid even in the cold.

* Pure benzoic acid may be wholly volatilised, and it leaves only a very trifling residue of charcoal; but if not pure, the residue of charcoal is more considerable.

* Benzoic acid may be easily recognized by its volatility and great solubility in alkalies, by its behaviour with peroxyde of iron, and especially by the property of being precipitated by acids from its alkaline solutions, provided they be not too dilute[1].

c. ACETIC ACID, $C_4H_3O_3$.

(Acide Acétique.)

* ACETIC ACID is a colourless liquid; when in the concentrated state it possesses a very pungent odour. Combined with the quantity of water, without which it cannot exist, it crystallises at a very low temperature. Alcohol dissolves it. It is completely

volatilisable. Its vapours, when it is concentrated, upon being set fire to, burn with a blue flame.

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[1] A mixture of alcohol, ammonia, and chloride of barium, producing no precipitate in solution of free benzoic acid, or of benzoates of alkalies, affords also a means of distinguishing succinic from benzoic acid.—ED.

* With most bases this acid forms salts which are soluble in water, and also in *alcohol;* even acetate of lead is soluble in alcohol. A few neutral acetates only are sparingly soluble.

* A solution of NITRATE OF SILVER is not troubled by free acetic acid; but it is rendered turbid by saturating the free acid with ammonia, or by employing the solution of a *neutral acetate,* in which case a crystalline precipitate of acetate of silver is formed, soluble in a large quantity of water with the help of heat, but which on cooling separates again from the liquor. This precipitate is insoluble in an excess of ammonia. When solution of neutral acetates are mixed with a solution of nitrate of silver, an abundant precipitate of acetate of silver is immediately determined, provided these solutions be not too dilute.

* A solution of SUBNITRATE OF MERCURY determines at once in acetic acid a crystalline precipitate of subacetate of mercury, which is dissolved by heating the liquor, but crystallises again when the liquor cools down. The influence of heat reduces part of the mercury, which circumstance imparts a somewhat greyish colour to the precipitate. Acetic acid, even diluted to a certain degree, produces this crystalline precipitate with subnitrate of mercury. When the solution of a *neutral acetate* is mixed with one of *subnitrate of mercury,* the formation of this precipitate of subacetate of mercury is more complete still.

* Acetic acid and the solutions of the neutral acetates do not reduce gold from a solution of PERCHLORIDE OF GOLD, even by heating the whole. But if an excess of solution of HYDRATE OF POTASH be added, a black precipitate of reduced gold is formed after some time.

* A solution of a neutral PERSALT OF IRON produces no perceptible change in acetic acid; but if the acid be saturated with ammonia, the liquor acquires a somewhat intense blood-red colour. The same effect is produced when a solution of neutral acetate is mixed with the solution of a neutral persalt of iron. The free acids, except acetic acid, destroy this blood-red colour,

and restore the yellowish tinge of the solution of the persalt of iron. An excess of ammonia precipitates the whole of the peroxyde of iron from the solution.

* CONCENTRATED SULPHURIC ACID, especially with the help of heat, disengages the acetic acid from the acetates, which may be recognized by its odour: the acid is not discoloured by heating.

FUMING SULPHURIC ACID disengages the acetic acid from the acetates, even in the cold, with a violent effervescence, and is not discoloured either by the influence of heat.

* The acetates are decomposed by a red heat; those, the base of which is an alkali or an alkaline earth, are converted, by being rapidly heated, into carbonates intermixed with charcoal. The metallic acetates often abandon their metal in the reduced state mixed with charcoal; or if the oxyde is of difficult reduction, it remains in the state of oxyde mixed with the charcoal. When acetates are submitted to distillation, the products always contain a mixture of acetic acid and of acetone in various proportions; the acetates with a strong base give very little of the first, and much of the second; the reverse is the case with the acetates which have a weak base.

* Free acetic acid may be recognized by its odour and volatility. It is detected in the solutions of its salts by their behaviour with PERSALTS OF IRON, and in the solid acetates by their deportment with CONCENTRATED SULPHURIC ACID[1]. The latter property distinguishes them more particularly from the lactates, which for a long time were looked upon as identical with the acetates, although in reality there is very little analogy, if any at all, between these two classes of salts[2].

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[1] Heating the acetates with a mixture of equal parts of sulphuric acid and alcohol is a better test than with sulphuric acid alone, because acetic ether is thus disengaged, the odour of which is much more characteristic.—ED.

[2] Of all non-volatile organic acids, acetic acid is the only one which has the property of dissolving protoxyde of lead in the state of a basic acetate of lead, which solution, when the protoxyde of lead is in excess, has an alkaline reaction on reddened litmus paper, and also on turmeric paper: this is therefore a characteristic test. Acetates being decomposed, as has been said, by concentrated sulphuric acid, must be mixed with it, distilled, and protoxyde of lead being digested, the product of distillation will, when tested by litmus paper, indicate whether acetic acid is present or not.—ED.

d. FORMIC ACID, C_2HO_3.

(Acide Formique.)

* FORMIC acid is a colourless liquid; its odour is pungent, but different from that of acetic acid; it is wholly volatile. When combined with only the smallest possible quantity of water, its vapour burns with a blue flame.

* With most bases it forms salts which are soluble in water; yet in general the formiates are less soluble than the corresponding acetates. A few amongst them dissolve in alcohol, but most of them are insoluble in this menstruum; such is the case with the formiate of baryta, for example, whilst the acetate of baryta is soluble in alcohol.

* A solution of ACETATE OF LEAD produces no precipitate in one of a formiate, provided the latter be not too concentrated; the addition of *ammonia* determines a slight precipitate.

* A solution of NITRATE OF SILVER produces immediately in the solution of a formiate a white crystalline precipitate of formiate of silver, which soon assumes a dark tinge, owing to a reduction of silver. Even in the cold this reduction is completely effected in course of time, and then a portion of the silver covers the sides of the vessel with a metallic coating; but this reduction proceeds more rapidly with the help of heat.

* A solution of SUBNITRATE OF MERCURY produces immediately in solutions of formiates a precipitate of formiate of mercury, which in the course of a few minutes, in the cold, becomes grey, owing to a mixture of reduced mercury; after the lapse of a certain time, even in the cold, the mercury is found reduced in the metallic state; heat much accelerates this reduction.

* When a solution of PERCHLORIDE OF GOLD is mixed with that of a formiate, the gold, even in the cold, is reduced, and the sides of the vessel become covered with a bright yellow coating. If, however, an excess of solution of HYDRATE OF POTASH be added before the reduction of the gold has begun, the metal is separated under the form of a black precipitate.

* A solution of neutral PERSALT OF IRON into which one of a formiate is poured, assumes a blood-red colour similar to that which solution of an acetate determines. Free acids destroy this colour. If *ammonia* be added, the whole of the peroxyde of iron is precipitated from the solution.

* CONCENTRATED SULPHURIC ACID, heated in conjunction with the formiates, gives rise to a disengagement of carbonic oxyde gas, which, being set fire to, burns with a blue flame, but in the cold this reaction does not take place; the acid remains colourless.

FUMING SULPHURIC ACID reacts on the formiates in the same manner, but the evolution of the gas is more violent, and this effect is produced even in the cold. It does not turn brown by heating.

* The formiates of fixed alkalies, for example, of baryta, strontia, or lime, disengage by exposure to a red heat a gas which burns like carbonic oxyde, and become converted into carbonates mixed with charcoal[1]. Those, the base of which is an easily reducible metallic oxyde, for example, OXYDE OF COPPER, oxyde of lead (*oxyde plombique*), are converted into the pure metal with a disengagement of carbonic acid, and of a less quantity of combustible gas.

* Formic acid and the formiates have much analogy with acetic acid and the acetates. They may, however, be distinguished from each other in more ways than one, and in general formic acid is more easily detected than any other. The points of resemblance of formic acid with acetic acid are its volatility and its behaviour towards persalts of iron, but it differs from it by the behaviour of its salts with CONCENTRATED SULPHURIC ACID, and by the extreme facility with which the formiates of mercury and of silver are reduced[2].

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[1] This inflammable gas is carburetted hydrogen.—ED.

[2] If a formiate be heated with a mixture of equal parts of sulphuric ether and alcohol, formic ether is disengaged, which has a peculiar and characteristic smell. —ED.

C. NITROGENISED ORGANIC ACIDS.

* CARBON, oxygen, hydrogen, and nitrogen, by combining together, form likewise a series of acids, few of which only are known, and which are principally met with in animal substances. Among these we may name, for example, *uric* and *uro-benzoic acid*. Some of these acids contain no hydrogen; in some others the proportion of the nitrogen, compared to that of the carbon, is the same as in cyanogen, such as *fulminic acid, cyanic* and *cyanuric acids*.

* As, however, these acids and their combinations are only very rarely met with in analytical researches, and several of them have been as yet examined with care by only a few chemists; we shall not indicate here their properties, nor their behaviour towards re-agents.

CHAPTER II.

HYDRACIDS.

1. MURIATIC ACID, Cl.+H.

(Acide Chlorhydrique.)

* PURE muriatic acid is a colourless gas, which cannot be condensed into a liquid, except by a strong pressure, and a considerable degree of cold. Muriatic acid gas has a suffocating acid odour and taste, forming dense fumes in the air; it is incombustible. It is soluble in water in extremely large quantity, and with violence. The saturated solution which constitutes the liquid concentrated muriatic acid is colourless; sometimes it has a yellowish or yellow tinge, which is due to the presence of organic substances, but more frequently to that of perchloride of iron. This solution emits fumes in the air, but it loses this property by dilution with water. Muriatic acid has a very strong and corrosive acid taste; ebullition deprives it of most of its muriatic acid gas, and this in proportion to its higher state of concentration. Very dilute muriatic acid does not lose its gas by ebullition, but on the contrary it renders it to a certain degree more concentrated; but even when this acid is very dilute, it produces white fumes when a rod of glass previously dipped in ammonia is held at its surface.

* NITRIC ACID decomposes muriatic acid by robbing it of its hydrogen; this decomposition, however, is better effected with the help of heat than in the cold. The mixture of muriatic and of nitric acid, ordinarily called *aqua regia*, contains therefore free chlorine after having been heated, owing to which aqua

regia has a yellow colour. It is also the presence of chlorine which imparts to aqua regia the property of dissolving gold and platinum, which metals are not acted upon by metallic or by nitric acid alone. Hydrochloric acid may therefore be recognised also by the property it possesses of dissolving gold after addition of nitric acid.

* SULPHURIC ACID does not decompose muriatic acid, even in the concentrated state.

* If muriatic acid be treated by PEROXYDE OF MANGANESE, RED LEAD, or PUCE OXYDE OF LEAD, (*suroxyde plombeux*, or *suroxyde plombique*), gaseous chlorine is disengaged, especially if heat be applied, which gas may be recognised as such by its colour, odour, and bleaching property [a slip of moistened litmus paper held over it is bleached].

* Muriatic acid converts the metallic oxydes into METALLIC CHLORIDES, which some chemists consider as being MURIATES when dissolved in water. In effect, these metals, the oxydes of which act as a base, always present, when combined with chlorine, the same properties which are characteristic of the combination of their oxydes with oxacids, as well in the dry state, as in that of aqueous solution. Wherefore in the first section of this volume devoted to the examination of the behaviour of the bases and their salts towards re-agents, we have always spoken of the metallic chlorides, although, properly speaking, we had to examine only the behaviour of the oxysalts.

* The chlorides of the metals, the oxydes of which act as acids, and not as bases, are the only ones which possess other properties. In the pure state these form generally volatile liquids; sometimes, however, they are solid or gaseous. They are soluble in water, manifestly undergoing decomposition at the same time, and disengaging much heat, in which case muriatic acid is always formed, and generally an oxyde of the body which was combined with the chlorine is produced, which acts the part of an acid: there are only a few circumstances in which a portion of this last body remains undissolved. But the decomposition of the volatile chlorides, by means of water,

is never effected in such a way, that, independently of the muriatic acid formed, chlorine is at the same time set at liberty. Chloride of tellurium, chloride of selenium, and chloride of sulphur are the only ones which are decomposed by water in such a manner, that a portion of the tellurium, of the selenium, and of the sulphur is liberated. Among these combinations we may name perchloride of tin, chloride of aluminum, chloride of glucinium, chloride of titanium, chloride of antimony, chloride of tungsten, chloride of molybdenum, protochloride of arsenic, chloride and perchloride of tellurium, chloride and perchloride of selenium, chloride and perchloride of phosphorus, chloride of silicium, chloride of boron, and chloride of sulphur. Amongst these compounds, chloride of aluminium, of glucinium, of antimony, perchloride of tungsten, of molybdenum, of tellurium, of arsenic, of selenium, of phosphorus, are solid at the ordinary temperature; perchloride of boron alone is gaseous, the others are liquid at the ordinary temperature, and several of them are extremely volatile.

* Some of the volatile chlorides cannot be isolated, but they form with the oxydes of the same metal compounds which have much resemblance with the pure chlorides, especially as regards their deportment with water. In effect, their aqueous solution contains, like that of the pure chlorides, muriatic acid, and the oxyde of the metal which dissolves as an acid. It is only by heating the vapours of these combinations to a temperature which exceeds that under the influence of which they are formed, that the oxydes sometimes separate after having lost their oxygen, and having been thereby converted into a lower degree of oxydisement. Such is the case with the chromate of chloride of chromium, of the tungstate of chloride of tungsten, of the molybdate of chloride of molybdenum; the first is liquid, the two others are solid.

* The aqueous solution of the metallic chlorides behave with re-agents nearly in the same manner as free muriatic acid.

* A solution of NITRATE OF SILVER, or of another soluble salt of silver, produces in these solutions a white precipitate of

chloride of silver, which, when in large quantities, has a curdy appearance, and which by exposure to the air becomes dark-purple at the surface. This precipitate is insoluble in dilute nitric acid, but is easily dissolved by ammonia, and if an acid be poured in such a solution, it is reprecipitated. It is dissolved with the help of heat by a pretty large quantity of very concentrated muriatic acid, but it is completely separated from the acid by simply diluting it with water. The soluble metallic chlorides, like free muriatic acid, may be easily recognised by this precipitate; and nitrate of silver is the most important of all re-agents to detect their presence; for nearly all the precipitates which the salts of silver determine in the solution of other salts, are soluble in dilute *nitric acid*, with the exception of the *bromate*, *bromide*, *iodate*, and *iodide of silver*, which, like *chloride of silver*, are not soluble in this re-agent. Chloride of silver may be distinguished from bromate and iodate of silver by the means which have been indicated before[1] (page 255), and the process for distinguishing it from bromide and iodide of silver will be explained farther on. The smallest quantities of a chloride in solution of free muriatic acid, may be detected by means of NITRATE OF SILVER; yet when the quantity is exceedingly minute, instead of a precipitate, an opaline tinge only is produced by it.

* The only precipitates which, besides those produced by *nitrate of silver*, are formed in solutions of metallic chlorides, or of free muriatic acid, are those which owe their production to the acid, and not to the basic element, such as for example, the precipitates formed by the solutions of SUBSALTS OF MERCURY, and, when the solutions of the chlorides are not too dilute, by SOLUTIONS OF OXYDE OF LEAD; for, except chloride of silver, subchloride of mercury, chloride of lead, and subchloride of copper, all the other chlorides are freely soluble in water. Yet several metallic chlorides form with the oxydes combinations

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[1] Chloride of silver fuses without decomposition at a temperature below red-heat, and forms a transparent mass after cooling, which character distinguishes it from cyanide of silver.—ED.

which are insoluble in water. These combinations are generally soluble in acids, and the presence of the metallic chloride may subsequently be discovered in the solution by pouring a solution of *nitrate of silver* therein. Dilute nitric acid may likewise be employed for dissolving the combination, but it is necessary in such a case to operate in the cold.

* If insoluble, or sparingly soluble, but non-volatile metallic chlorides be mixed with carbonate of soda or of potash, such as, for example, *chloride of silver* or of *lead*, and the whole be strongly ignited in a small porcelain crucible, a chloride of potassium or of sodium is formed; and if the chloride experimented upon be one of silver, metallic silver is obtained at the same time with disengagement of oxygen and of carbonic acid; and if the chloride be one of lead, carbonate of lead is obtained, besides the chloride of potassium or of sodium. If the ignited mass be treated by water, the chloride of potassium or of sodium, as well as the excess of carbonate of alkali, is dissolved, so that if the solution be supersaturated by nitric acid, solution of *nitrate of silver* will produce therein a precipitate of chloride of silver. This is a certain method of detecting the presence of chlorine in the insoluble or sparingly soluble chlorides, and of separating it therefrom.

* When concentrated SULPHURIC ACID is poured upon the metallic chlorides in the solid state, and the mixture exposed to heat, most of them disengage muriatic acid gas with effervescence. The minutest quantities of this gas produce white clouds when a glass rod moistened with liquid ammonia is held at the surface. If the experiment be performed in a tube of white glass closed at one end, it may be perceived that the gas disengaged is colourless. There are only a few metallic chlorides which, when thus treated with sulphuric acid, resist decomposition; amongst these we must place *subchloride of mercury* (calomel), *protochloride of mercury* (sublimate), and *protochloride of tin*. Protochloride of mercury (corrosive sublimate) dissolves in hot sulphuric acid without undergoing decomposition, and crystallises in the midst of the liquor as it cools. Subchloride of mercury

is converted by hot sulphuric acid into protochloride and sulphate of mercury (*sulphate mercurique*), with disengagement of sulphurous acid. Protochloride of tin deoxydises sulphuric acid.

* The concentrated solutions of the other acids which are but slightly volatile or fixed, act in the same way as sulphuric acid.

* If the metallic chlorides be triturated with some CHROMATE OF BICHROMATE OF POTASH, the mixture introduced into a tubulated retort, and concentrated, but preferably fuming sulphuric acid be poured upon it, and the whole be exposed to a moderate heat, a blood-red coloured gas, condensing into a liquor, distils over, which is a chromate of perchloride of chromium; treated by an excess of liquid ammonia, a solution is obtained which is of a yellow colour, owing to the presence of chromate of ammonia[1].

* When the metallic chlorides are treated by PEROXYDE OF MANGANESE, RED LEAD, OF PUCE OXYDE OF LEAD, (*suroxyde plombeux*, or *suroxyde plombique*), and CONCENTRATED SULPHURIC ACID is poured upon the mixture, and heat is applied, chlorine gas disengages, which is recognisable by its characteristic odour and colour. If this gas be abundantly disengaged, it bleaches moist litmus paper.

* Several metallic chlorides, but not all, are decomposed when boiled for a long time with an excess of NITRIC ACID. Chlorine gas is disengaged pending the operation, and if the free acid be evaporated, a nitrate is left behind.

* Most of the combinations of chlorine with those metals, the oxydes of which act like a base, are not decomposed by being exposed to a red heat out of the contact of the air. But a very

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[1] This is in fact the test for detecting the presence of a *chloride* in a substance which at the same time contains a *bromide*, for both produce the blood-red liquid just mentioned; but if this liquid, being mixed with solution of ammonia, produces a yellow solution of chromate of ammonia, which becomes of a red-yellow colour by the further addition of an acid, owing to the formation of a bichromate of ammonia, the presence of a chloride is certain; for if a bromide only were present, the blood-red liquid above-mentioned would be bromine, which an excess of ammonia would render colourless, instead of yellow.—ED.

great number of them, by being ignited in the air, undergo a partial decomposition which is generally determined by the moisture of the air; in such a case an oxyde is formed, and muriatic acid gas is disengaged, and the residuum is more or less insoluble in water. The *chlorides* of the *alkalisable metals,* and likewise the *chlorides of barium* and *strontium,* do not undergo this change. *Chloride of lime* is not materially decomposed, a very small portion excepted. The chlorides of the alkalisable metals are more easily volatilised in part when heated in the air than when heated in close vessels.

* Both the soluble and the insoluble metallic chlorides may, according to Berzelius, be recognised before the blow-pipe in the following manner:—Take a small quantity of the chloride and add it to a fused bead of oxyde of copper and microcosmic salt, and direct the flame of the blow-pipe upon the whole, when the bead will be seen surrounded by a beautiful blue flame. For this experiment microcosmic salt quite free from chloride of sodium, or any other chloride, must be taken.

* Free muriatic acid and the soluble metallic chlorides behave towards solution of *nitrate of silver* in such a peculiar manner, that they cannot be confounded with any other substance of which we have hitherto been treating. The insoluble metallic chlorides are very easily recognised as such before the blow-pipe, or else the chlorine which they contain may be separated by fusion with alkaline carbonate.

2. HYDROBROMIC ACID, BrH.

(Acide Bromhydrique.)

* HYDROBROMIC acid is a gas which very much resembles muriatic acid gas. Hydrobromic acid gas emits in the air white fumes which are denser than those produced by muriatic acid gas. It is decomposed by chlorine gas which deprives it of its hydrogen, and sets the bromine at liberty, which then appears under the form of reddish vapours, or if in more considerable proportions, it condenses into drops of a similar colour. Hydro-

bromic acid gas is extremely soluble in water; the solution is colourless, and, both in the concentrated or in the dilute state, it very much resembles concentrated or dilute muriatic acid. When, however, hydrobromic acid gas contains any free bromine, the liquid acid has a dark reddish colour.

* The concentrated solution of hydrobromic acid gas in water parts with some of its gas when subjected to boiling, an effect which does not take place with the dilute solutions. Bromhydric acid which is saturated with free bromine, loses it, and at the same time a portion of hydrobromic acid gas, by boiling; there remains a dilute acid which is colourless[1].

* An aqueous solution of CHLORINE, or a current of chlorine gas, imparts a red colour to liquid hydrobromic acid, because bromine is thereby liberated.

* NITRIC ACID does not react promptly upon hydrobromic acid, but by heating the mixture, bromine is immediately set free, and a liquid is thus obtained similar to *aqua regia*[2].

* SULPHURIC ACID may also, by reacting with the help of heat upon concentrated hydrobromic acid, rob it of its hydrogen, in which case there is a disengagement of sulphurous acid produced.

* PEROXYDE OF MANGANESE, and also RED LEAD ($PbO + PbO_2$), and PUCE OXYDE OF LEAD, produce a disengagement of gaseous bromine and hydrobromic acid, when heated in contact with this acid.

* Hydrobromic acid forms with the metallic oxydes, ***metallic bromides,*** which in many respects resemble the metallic chlorides. The combinations of bromine with the metals the oxydes of which act as a powerful acid, are volatile, but always less than the corresponding chlorides, which they resemble in respect to their behaviour towards water.

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[1] Hydrobromic acid can dissolve so large a proportion of bromine that the solution becomes as deep in colour as bromine itself, and is precipitated from this solution, according to M. Bineau, by water. When water ceases to produce a precipitate, the acid which remains is yellowish, and is combined with three equivalents of bromine.—ED.

[2] That is to say, that it dissolves gold and platinum.—ED.

* The solutions of the metallic bromides which are soluble in water are recognised when tested by the same properties which characterise free hydrobromic acid.

* A solution of NITRATE OF SILVER produces in these solutions a white precipitate of bromide of silver[1] insoluble in dilute nitric acid, but soluble in ammonia, though less so than chloride of silver, from which it is distinguished by a pale yellowish tinge, which disappears when muriatic acid is poured upon it. If a little CHLORIDE OF LIME be added, the liquor assumes a yellowish or reddish colour, according to the quantity of the bromide of silver produced. This colour is due to a liberation of bromine.

* A solution of SUBNITRATE OF MERCURY produces in solutions of metallic bromides and hydrobromic acid, a white precipitate with a tinge of yellow, which is subbromide of mercury.

* The solutions of OXYDE OF LEAD produce a white precipitate of bromide of lead insoluble even in a large quantity of water, a property by which it is distinguished from chloride of lead[2].

When NITRIC ACID is poured in solutions of metallic bromides and the whole is then heated, vapours of a reddish-yellow colour are disengaged, which are due to gaseous bromine. If the solution of the metallic bromide was colourless it acquires thereby a reddish-yellow, or when dilute, a yellow tinge. When the mixture is not subjected to heat, the solution of the metallic bromide undergoes no sensible change by treatment with nitric acid[1].

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[1] This precipitate of bromide of silver is white at first, but soon becomes dirty white or yellowish, insoluble in dilute nitric acid, but concentrated nitric acid can dissolve a small portion of it, which, however, is reprecipitated by addition of water. It is much more readily acted upon by light than chloride of silver, and exposure to it renders it almost immediately of a violet or black colour. It is very fusible, and the fused mass after cooling is of an intense and pure yellow colour.—ED.

[2] Though difficultly soluble in water, bromide of lead is not altogether insoluble therein, and on the other hand, the reader should recollect that the solubility of chloride of lead is diminished by the presence of other salts, especially that of chloride of calcium, or even of muriatic acid, which in fact produce a precipitate in the concentrated solution of chloride of lead. Both the *chloride* and the *bromide of lead* are easily fusible, but the *chloride of lead* after cooling forms a colourless or greyish-white, translucid, horn-like mass (*plumbum corneum*), whilst *bromide of lead* fuses into a red liquid, which, on cooling, assumes a fine yellow colour.—ED.

* If MURIATIC ACID be added to the solution of a metallic bromide, it (the bromide) becomes converted into a chloride with formation of hydrobromic acid, but the liquor remains colourless. If, however, the metallic bromide contains a small quantity of a bromate, as may occur when the experiment is performed upon the bromide of an alkalisable metal prepared by causing the alkali to react upon bromine, the liquor becomes yellow or brown from a liberation of bromine.

* When CHLORINE GAS is passed through the colourless solution of a metallic bromide, this solution assumes a reddish-yellow, or yellow colour, on account of the bromine which is set free. CHLORIDE OF LIME produces the same effect when added to the solution of a metallic bromide, previously rendered acid, for which purpose any acid may be employed.

* CHLORINE is the most delicate test to discover the slightest traces of metallic bromide or of hydrobromic acid, in solution or in a mixture of salts. In order, however, to be enabled to detect very minute traces of metallic bromide by means of this re-agent, it is necessary first to remove the bromine which is set free, by means of ether; the process is as follows:—The liquid or concentrated solution of the saline mixture is introduced into a vessel of white glass, susceptible of being well corked up, and ether is poured upon it in sufficient quantity to form, after briskly shaking the whole, a layer of about an eighth of an inch thick above the liquid; aqueous solution of chlorine gas is then to be carefully added, a few drops of which are sufficient, if there be only a small quantity of bromine, and the flask is to be corked up and shaken. When the ether has separated it will be found to have a brown tint, owing to the bromine it will have taken up, or if only a small quantity of bromine be present, the ether has a yellowish colour. If no bromine be present the ether remains colourless. By

prolonged contact the solution of bromine in the ether is converted into hydrobromic acid, and the ether becomes colourless, but a small quantity of aqueous solution of chlorine is sufficient to restore the colour. When, in this experiment, the ether appears so slightly coloured as to render the presence of bromine doubtful, it is advisable to submit the liquid under examination to a counter-experiment by means of a saline solution, which, it has been ascertained, contains no metallic bromide; it is to be treated in the same manner with the same quantity of chlorine and of ether, and it may be seen by comparison whether the former is quite colourless. If, instead of adding aqueous solution of *chlorine* to the liquor under trial, a current of *chlorine gas* is passed through it, a sufficient quantity of the latter gas may be dissolved, so as to impart a yellowish colour to the ether, and thus simulate the presence of bromine.

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[1] According to Dr. Fresenius, bromide of silver and perbromide of mercury are not decomposed by nitric acid.—ED.

* It should, however, be remarked here, that when no sensible quantity of bromine is found in a saline mixture tested as above, the mixture should be digested in alcohol, and the alcohol being subsequently evaporated the dry residuum must be dissolved in water, and this aqueous solution must be treated, as has been just said, by chlorine-water and ether.

* If a SOLUTION OF STARCH be poured in the colourless solutions of metallic bromides, to which nitric acid has been added, the liquor becomes brownish, but the production of this colour is not very characteristic; *starch* is employed to distinguish metallic bromides from metallic iodides, and not for the purpose of identifying the first of these compounds in solutions.

* Bromide of silver, bromide of lead, and other non-volatile bromides being mixed and fused with a CARBONATE OF ALKALI are decomposed like the corresponding chlorides, and a bromide of alkalisable metal is produced[1].

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[1] The volatilisable bromides are the following:—Bromides of cadmium, of zinc, of arsenic, of antimony, protobromide of copper, of nickel, of iron, and of bismuth. The following are soluble in water:—Bromides of lead, of silver, protobromides of copper, of mercury. Those of antimony and of bismuth are decomposed by water into a basic bromide which is deposited, whilst hydrobromic acid remains in solution.

* When the metallic bromides in the solid state are put in a tube of white glass closed at one end, and, CONCENTRATED SULPHURIC ACID being poured thereon, heat is applied, gaseous bromine is disengaged, which fills up the colder portion of the tube, and which may be easily recognised in daylight by its ruddy colour, similar to that of nitrous acid. This colour cannot be well seen by artificial light. Sulphurous acid and hydrobromic acid are formed at the same time. A few metallic bromides, for instance, protobromide of mercury, are not decomposed by *sulphuric acid*[1]. Instead of *sulphuric acid,* BISULPHATE OF POTASH may be employed and fused with the metallic bromide in a small glass tube closed at one end; besides sulphurous and hydrobromic acid, bromine vapours are evolved, which may be easily recognised by their colour.

* When metallic bromides are triturated with CHROMATE or BICHROMATE OF POTASH, and the whole is introduced into a tubulated retort, *concentrated sulphuric acid,* or preferably, fuming sulphuric acid, is poured upon it, and the whole moderately heated, a liquor of a blood-red colour distils over, which resembles that produced by the metallic chlorides when subjected to the same treatment, but which liquor, in the present case, is pure bromine, and which by an addition of excess of ammonia forms a colourless solution, which contains only hydrobromate of ammonia. If, however, the metallic bromide employed contained a small portion of metallic chloride, the ammonia has then a slightly yellowish tinge, which is due to some chromate of ammonia. This is the only method by which a mixture of a metallic chloride with a metallic bromide can be accurately detected[2].

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together with a small portion of bromide. Bromide of arsenic is decomposed by a large quantity of water into arsenious acid which is deposited, and hydrobromic acid which remains in solution. Protobromide of cadmium, of zinc, of nickel, of cobalt, are soluble in alcohol, ether, concentrated muriatic acid and ammonia.—ED.

[1] Berzelius says, that protobromide of mercury (*bromure mercurique*) is decomposed both by nitric and sulphuric acids. The same authority states, that bromide of copper is not acted upon by sulphuric acid.—ED.

[2] See the note, page 423.—ED.

* The metallic bromides seem to behave under the influence of heat like the metallic chlorides.

* Before the BLOW-PIPE a metallic bromide mixed with a globule of microcosmic salt holding oxyde of copper in solution imparts a blue colour to the flame, exactly as is the case with the metallic chlorides under similar treatment, though the flame produced by the bromides has a more greenish tinge.

* Solutions of hydrobromic acid, and the metallic bromides, are recognised by the precipitates produced therein by solutions of NITRATE OF SILVER and of SUBNITRATE OF MERCURY. Bromide of silver differs from all the precipitates produced by *nitrate of silver* in the solutions of the substances hitherto treated of, by its insolubility in dilute *nitric acid*; though in this respect *chloride, bromate,* and *iodate of silver* are exceptions. The method of distinguishing chloride from bromide has been indicated above (page 426). *Bromide of silver* differs from *bromate* and from *iodate of silver* by its yellow tinge, and because these being exposed to a red heat yield oxygen gas, which property is common to the bromates and iodates in general. The presence of bromine can be detected in the bromides which are insoluble in water by following the process which has been indicated in reference to the *bromide of silver* (page 427). The bromine which they contain may likewise be separated by fusing them with carbonate of potash.

3. HYDRIODIC ACID, IH.

(Acide Iodhydrique.)

* PURE hydriodic acid is gaseous. Hydriodic acid gas resembles muriatic and hydrobromic acid gases; but it is more easily decomposed than these by the substances which have an affinity for hydrogen. It is more easily decomposed than the two latter gases when treated by certain metals, which combine with the iodine and disengaged hydrogen gas, as mercury, for instance.

* Hydriodic acid gas is extremely soluble in water. The solution is colourless, and resembles that of muriatic and hydro-

bromic acids. When boiled, it disengages hydriodic acid, and becomes weaker. By exposure to the air it assumes a yellow, then gradually adark-brown colour; the hydrogen being oxydised by the air, the iodine which is thus liberated is dissolved by the portions of acid which have not as yet suffered decomposition.

* CHLORINE, NITRIC ACID, SULPHURIC ACID, and the METALLIC PEROXYDES alter liquid hydriodic acid in a similar manner as the solutions of metallic iodides, of which we shall soon have to speak.

* Hydriodic acid forms METALLIC IODIDES with the corresponding metallic oxydes. These compounds resemble in many respects the metallic chlorides and bromides; yet most of the metallic iodides differ from them by their insolubility in water. It is only the iodides of alkalies, of earths, and a few others, which are soluble in water[1]. The metallic iodides which are insoluble in water have often a characteristic colour, wherefore the solution of IODIDE OF POTASSIUM is employed as a re-agent to detect certain metallic oxydes in solution, wherefore the behaviour of solutions of *iodide of potassium* towards these oxydes has been mentioned. The solution of *iodide of potassium* is not, however, a re-agent to be trusted in all cases, because the precipitates which it determines are more or less soluble in the liquor in which they are produced. The combinations of iodine with the metals the oxydes of which form powerful acids, are volatile, but much less so than the corresponding combinations of bromine and of chlorine.

* A solution of NITRATE OF SILVER produces in the solution of metallic iodides, a white precipitate of iodide of silver, which has a yellowish tinge. By this precipitate the solution of metallic iodides and hydriodic acid may be recognised, because, like chloride, bromide, and bromate of silver, it is insoluble in dilute nitric acid, but it differs from these three compounds, because it is almost insoluble in free ammonia. When the

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[1] The iodides of zinc and of iron are soluble in water; the first forms a colourless, the second a green solution. Iodide of cobalt dissolves in water, with which it forms a red solution.—ED.

solution of a metallic iodide contains, at the same time, a metallic chloride, the presence of the iodide may be very easily recognised, because the precipitate produced by the solution of *nitrate of silver* is almost insoluble in ammonia, though in such a case the operator runs the risk of overlooking the presence of the metallic chloride. The best thing to be done then is to add an excess of ammonia to the liquor in which the solution of *nitrate of silver* has produced a precipitate, and then to supersaturate with dilute nitric acid the liquor which will have been filtered from the precipitate of iodide of silver produced. If an abundant precipitate is thereby produced in the filtered liquid, it is a proof that the solution of the metallic iodide contained at the same time a metallic chloride; if, on the contrary, a very feeble precipitate is produced, or rather if the liquor only becomes slightly opaline, one may conclude therefrom that the liquor either contained no metallic chloride, or at any rate a very small quantity only. When a metallic iodide contains a metallic bromide, the presence of the latter may be recognised in the same way.

* The method of distinguishing the solutions of metallic iodides by means of solutions of salts of lead or of mercury, or of other metallic oxydes, has been already indicated (pages 99—139, and elsewhere).

* If moderately strong NITRIC ACID be added to the solutions of the metallic iodides and of hydriodic acid, they become yellow, and if the mixture be heated, it assumes a reddish-brown colour; violet fumes of iodine are evolved, and, after cooling, iodine is found deposited under the form of black, shining spangles.

* When MURIATIC ACID is poured in the solution of a metallic iodide, it becomes converted into a metallic chloride with formation of hydriodic acid; but the liquor at first remains colourless. If, however, the metallic iodide contains a little iodate, which may happen when the iodide is one of an alkalisable metal, produced by causing iodine acid to react upon alkali, an abundant precipitate of iodine is formed in the liquor, which after a short time is deposited.

* When aqueous solution of CHLORINE is poured in solutions of metallic iodides, or in hydriodic acid, they become immediately of a reddish-brown colour, and a larger addition of aqueous chlorine renders them limpid again as before. The same effect takes place when CHLORIDE OF LIME or a little dilute muriatic acid is added to the solution of a metallic iodide.

* When a solution of STARCH in boiling water is added to the solution of a metallic iodide, or to hydriodic acid, no change is observed, but if a little *nitric acid* be subsequently added to the liquor it assumes a fine blue colour. This colour is so intense, that it appears black if the quantity of iodine be considerable. Free iodine is the only substance which can produce this blue colour with starch, and when combined with hydrogen or with metals it cannot produce it; wherefore the blue colour is determined by *starch* in hydriodic acid or in solutions of metallic iodides only by the addition of another substance by which iodine may be liberated, as, for example, by *nitric acid*. Aqueous solution of *chlorine* produces also this characteristic blue colour in these solutions, but an excess of this re-agent causes it to disappear[1]. If much *arsenious acid* be present, the blue colour is not produced in the preceding cases, but its appearance may be determined by pouring in the liquor a few drops of somewhat dilute nitric acid. If in the solution of a metallic iodide a sufficient proportion of protochloride of mercury (*corrosive sublimate*) is poured to cause the precipitate of iodide of mercury produced to re-dissolve in the excess of protochloride of mercury, no blue colour is determined when subsequently nitric acid and a solution of starch is poured in the liquor, nor can it, in such circumstances, be produced by the addition of sulphuric acid. When a liquor contains a small quantity of hydriodic acid or of metallic iodide, and at the same time much muriatic acid or metallic chloride, the addition of solution of *starch* and of *nitric acid* determines the blue colour in the cold, but this colour disappears by heating the liquor. The blue colour of the

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[1] This is owing to the excess of chlorine combining with the iodine and forming a colourless *chloride of iodine*.—ED.

combination of iodine and starch which has been produced, is destroyed by the solutions of alkalies, by sulphurous acid, phosphorous acid and sulphuretted hydrogen, &c., but may be restored by nitric acid. When an excess of aqueous solution of *chlorine* has been poured in a solution of iodic acid or of a metallic iodide, or in hydriodic acid, the solution of starch determines the production of the blue colour in the mixture only after the addition of a little *protochloride of tin, sulphurous acid, sulphuretted hydrogen,* or other reducing bodies. By strict attention to the above precepts, the solution of *starch* may be the means of detecting the minutest traces of hydriodic acid, or of metallic iodides in solutions. A small quantity of *starch* does not produce a blue colour but one of a deep green hue in a solution which contains a large proportion of iodine, or after addition of nitric acid in a saturated solution of hydriodic acid or of a metallic iodide.

* If, by following the above process, no sensible trace of iodine has been detected in a saline mixture, this mixture should be digested in alcohol, and after evaporating the alcohol, the dry residuum should be dissolved in a little water, and this solution tested for iodine by the process above alluded to.

* When *iodide of silver, iodide of lead,* or other non-volatilisable metallic iodides are mixed and fused with a carbonate of alkali, they are decomposed, as is the case with the corresponding metallic chlorides, and an iodide of alkalisable metal is formed.

* When after having introduced metallic iodides in the solid state into a tube of white glass, closed at one end, CONCENTRATED SULPHURIC ACID is poured upon them, and the whole is heated, gaseous iodine is evolved, which fills up the colder portion of the tube, and which is easy to detect by its characteristic violet colour. At the same time, sulphurous acid and even sulphuretted hydrogen gas are formed, but no hydriodic acid. Even those metallic iodides whose corresponding chlorides and bromides cannot be decomposed by concentrated *sulphuric acid,* for example, protoiodide of mercury (*iodure mercurique*), are decomposed by this process. If the metallic

iodide be mingled with PEROXYDE OF MANGANESE, RED LEAD, or with PEROXYDE OF LEAD, upon heating the mixture with *sulphuric acid*, gaseous iodine only is evolved, but no sulphurous acid. Sulphuric acid likewise determines a similar decomposition in the concentrated solution of metallic iodides and of hydriodic acid. The iodine which is thus liberated imparts then to that liquor a yellow colour in the cold, and a reddish-brown colour when heated: this phenomenon is less apparent in very dilute solutions.

* BISULPHATE OF POTASH may be substituted for sulphuric acid by proceeding as for the detection of a metallic bromide (page 429). During the fusion, fumes of iodine are evolved, which are easily recognisable as such by their colour.

* When metallic chlorides are treated by CHROMATE or BICHROMATE OF POTASH and SULPHURIC ACID, iodine only is disengaged. In treating in the same way a mixture of iodide and chloride of metals, no chromate of chloride of chromium is obtained (page 423); but at first, gaseous chlorine is disengaged, followed some time afterwards by fumes of iodine, but no chloride of iodine is even formed. It is only when the metallic chloride predominates much that the formation of chromate of chloride of chromium is determined.

* The combinations of iodine with the metals of alkalies are not decomposed by being heated in the air; by a very strong heat they are volatilised, and as is the case with the corresponding chlorides, their volatilisation is more easily effected with, than out of the contact of the air. Most of the other metallic iodides undergo partial decomposition by exposure to a red heat in the air. Ordinarily, in such cases, purple fumes of iodine are evolved, and an oxyde remains.

* Before the BLOW-PIPE, metallic iodides upon being heated with a bead of microcosmic salt holding protoxyde of copper in solution, impart to the flame a fine emerald-green colour.

* When iodine is combined with a metal and the combination is soluble in water, the best means of detecting iodine is to resort to nitric acid and the solution of starch. Iodine may

thus be detected in all kinds of solutions, even when the liquor contains several other substances, though the operator must bear in mind that their presence may form an obstacle to the manifestation of the blue colour. When, on the contrary, the combination in which iodine is sought for is insoluble in water and in dilute nitric acid, the best method is to treat it by concentrated *sulphuric acid,* in order to obtain the purple fumes of iodine. It is advisable in such cases to add a little peroxyde of manganese to the substance, in order to prevent the formation of sulphurous acid. If the iodine be in too small proportion manifestly to produce purple fumes, its presence may be ascertained by mixing the compound with manganese, introducing the whole in a flask and pouring sulphuric acid upon it; if a piece of paper, smeared over with starch be now introduced into the empty portion of the flask, it will, after some time, assume a blue colour, even if the compound contain only extremely minute traces of iodine. The best method is to fix the above paper between the neck of the flask and the cork.

4. HYDROFLUORIC ACID, FH.

(*Acide Fluorhydrique.*)

* HYDROFLUORIC ACID is, in the pure state, a colourless liquid[1], which even at the ordinary temperature of the air is converted into a colourless gas of a strong penetrating odour, and exceedingly soluble in water. The aqueous concentrated solution emits dense white fumes in the air. By ebullition it loses the greatest part of the hydrofluoric acid, and a weaker acid remains.

* Aqueous hydrofluoric acid is not decomposed by SULPHURIC nor by NITRIC ACIDS, nor by CHLORINE GAS. That which especially distinguishes it from all other acids, is its property of dissolving silica, and consequently, of attacking glass; wherefore,

the experiments to which it is submitted cannot be performed in glass vessels. The best way is to employ platinum utensils.

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[1] It often occurs, however, that the fluor-spar from which hydrofluoric acid is obtained is contaminated by sulphuret of lead, which decomposing the water of the sulphuric acid employed in the preparation, produces sulphuretted hydrogen and sulphurous acid, in which case the hydrofluoric acid obtained is turbid or milky from the presence of sulphur, which, however, in a short time is deposited.—ED.

Hydrofluoric acid forms with the metallic oxydes, *metallic fluorides*, most of which may be distinguished from the corresponding chlorides by their less solubility in water. The combinations of fluorine with the metals of the alkalies are very sparingly soluble in the pure state; those of fluorine with the metals of the alkaline earths are either altogether insoluble or very sparingly soluble; lastly, those of fluorine with the metals, properly so called, are not generally very soluble; a few of these are, however, more soluble than the corresponding chlorides. Several of these metallic fluorides combine with hydrofluoric acid, and are thereby rendered soluble; but some of them are altogether insoluble in that acid. The combination of fluorine with the metals, the oxydes of which form powerful acids, are partly very volatile and are often unknown under any other form than the gaseous state, such is the case, for example, with *fluoride of silicium*, and *fluoride of boron* (*fluoride silicique* and *fluoride borique*.)

* The SALTS OF LIME especially produce precipitates in the solutions of metallic fluorides. If a solution of CHLORIDE OF CALCIUM be poured in that of a very pure metallic fluoride, a gelatinous mass is obtained which is so translucid that, at first, the operator is led to think that only a very small precipitate will be obtained. The precipitate of fluoride of calcium thus produced does not settle well except after addition of *ammonia*, and then a very voluminous precipitate is most distinctly formed This precipitate is soluble in nitric and in muriatic acids, but in exceedingly small proportion only. If, however, the metallic fluoride contains silica, the fluoride of calcium produced is much more easily soluble in these acids, from which solution it may be re-precipitated by ammonia. Fluoride of calcium is only very slightly soluble in free hydrofluoric acid.

* Fluoride of silver being soluble in water, the solution of NITRATE OF SILVER does not trouble hydrofluoric acid, nor the solutions of metallic fluorides. The solution of subnitrate of

mercury produces no precipitate in hydrofluoric acid; but ACETATE OF LEAD determines a precipitate therein.

* An easy and certain method of detecting the minutest quantities of metallic fluorides in the solid state consists in pouring CONCENTRATED SULPHURIC ACID upon them, and heating the whole in a platinum crucible; hydrofluoric acid is thus disengaged, the minutest traces of which become evident by their corrosive action upon glass. It is necessary to heat the platinum crucible because several metallic fluorides, for example, *fluoride of calcium,* are soluble in cold concentrated *sulphuric acid,* and thus produce a viscid, stringy, translucid liquor without any hydrofluoric acid being liberated; but by heating the whole, hydrofluoric acid is disengaged and the residuum is a sulphate. In order to ascertain the presence of the hydrofluoric acid, which is disengaged, the platinum crucible is to be covered with a plate of glass coated with wax on which some writing has been traced. The wax coating is applied to the glass by heating it, and fusing a little wax upon it. When the glass plate has become cold, the writing is to be traced upon the wax with a needle or wire of soft iron, taking care that the instrument penetrates down to the glass[1]: this done, as soon as the concentrated sulphuric acid has been poured upon the metallic fluoride under examination, the platinum crucible is to be covered with the waxed side of the glass plate, and by holding it at the top of the flame of a spirit-lamp, heated gently enough not to melt the wax. A small quantity of water may also be poured over the outside of the glass plate in order more securely still to prevent the fusing of the wax. The crucible is now suffered to cool, and the wax is next to be scraped off, when the glass will be found corroded at the points occupied by the writing. A few milligrammes of metallic fluoride are sufficient[2] to render the corrosion of the glass manifest, but if the quantity of metallic fluoride be too inconsiderable, the corrosion of the glass becomes

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[1] It is better to use a pointed rod of brass, such as a common pin, or even one of lead, in order to prevent all chance of scratching the glass.—ED.

[2] The milligramme is ·0154 of the English grain.—ED.

apparent only when after removing the wax it is breathed upon.

* If a platinum crucible is not at hand, the metallic fluoride is to be reduced to powder, and made into a paste with concentrated sulphuric acid, in which state it is to be applied upon the wax-coated plate of glass, upon which the writing has been traced. After standing thus for a long time, the wax may be scraped off, and the corrosion of the glass at the point occupied by the writing may be perceived. In order to succeed, it is, however, necessary to use a pretty large quantity of fluoride.

* In the same way, and by means of sulphuric acid, metallic fluorides may be detected in solutions which are not too dilute. If the solution of the metallic fluoride is a dilute one, it is necessary, after having added the sulphuric acid to the liquor, to pour it in a glass the inside of which is coated with wax and on certain portions of which some writing has been traced; the solution, if the quantity be not too considerable, is then left to evaporate to dryness in the glass. When afterwards the dried mass is removed by washing and the wax coating is scraped off, it may be seen that the glass has been attacked in those parts corresponding to the writing. If only a very small quantity of a solution containing a minute portion only of metallic fluoride is in the operator's possession, the liquor, according to Berzelius, may be evaporated upon a watch-glass. It is necessary, however, that this glass be of such a quality as to resist the action of the ordinary acids. When afterwards the dry saline mass is dissolved with water, it may be seen that the glass has been manifestly corroded at the place corresponding to that occupied by the residuum. The safest method, however, of detecting the presence of a metallic fluoride is that first indicated, and which consists in treating the dry compound by sulphuric acid in a platinum crucible. It is best, therefore, when the object is to search for hydrofluoric acid, or a metallic fluoride in a very dilute neutral or alkaline solution, to evaporate it to dryness in a platinum crucible, and to treat the dry mass by sulphuric acid

as has been said. If the solution be acid, it must be first saturated by ammonia, and treated as has just been said.

* All metallic fluorides are decomposed when heated with sulphuric acid. There are compounds, however, which contain metallic fluorides amongst their constituent principles, and which are not decomposed by sulphuric acid with the help of heat. The presence of hydrofluoric acid in such compounds cannot, therefore, be detected by the process which we have just described, even though the compound may contain a considerable quantity of it. Several siliceous compounds found in nature, such as topaz, belong to this category. The presence of fluorine may be detected therein by means of the BLOW-PIPE, as will be indicated below; yet this means does not always succeed when the proportion of fluorine is very minute, as in some species of amphibole.

* The following is the least dubious process to detect the presence of fluorine in compounds which sulphuric acid cannot decompose. The compound is to be reduced into fine powder by trituration and levigation, and mixed with about three or four times its weight of carbonate of soda, and strongly ignited in a platinum crucible; the calcined mass is then to be softened with water, and the solution is separated from the insoluble portion by throwing the whole upon a filter. If too large a quantity of solution has been obtained, it must be evaporated in a porcelain capsula until it be reduced to a convenient bulk, it is then to be poured in a platinum capsula, or if no such vessel is at hand, in one of pure silver, and it is to be cautiously saturated with muriatic acid. For stirring it, a rod of silver or of platinum must be used, and not one of glass. The acid liquor is to be left at rest for a long time, in order to allow of the carbonic acid being disengaged as much as possible in the cold, and it is then to be supersaturated with ammonia in the capsula. The ammoniacal liquor is then poured in a glass flask, and mixed therein with *chloride of calcium*, and the flask being now closed with a cork, a precipitate of fluoride of calcium will be formed if the compound contained a metallic fluoride. The *fluoride of*

calcium is to be precipitated in a corked flask, because by thus excluding the contact of the air it cannot be sensibly contaminated with carbonate of lime. The liquor is then to be filtered, and, after drying the precipitate, it is to be decomposed by sulphuric acid in a platinum crucible, as previously indicated, in order positively to ascertain that it really consists of fluoride of calcium.

* The combinations which consist essentially of a metallic fluoride as, for example, fluor-spar and topaz, are precisely those in which the presence of the fluoride is most difficult to detect by means of the blow-pipe. It is, on the contrary, more easy to recognize it in the compounds which contain only a very minute quantity of it, and in which this salt seems in fact to be an accidental ingredient, as, for example, in some varieties of mica, when these compounds contain at the same time a little water[1]. In order to detect the presence of the metallic fluoride in the first of these combinations, they should be mixed with some microcosmic salt previously fused, and heated at the extremity of an open glass tube in such a way that part of the flame be pushed into the tube by the current of air. Some aqueous hydrofluoric acid is thus formed which flows along the tube, and which may be recognised, not only by its peculiar odour, but also because it corrodes the glass tube in its whole length, but principally at those points where moisture had deposited. If then a brazil-wood test paper, moistened with water, be introduced into the coldest part of the tube, it becomes yellow. According to Bonsdorff, this property of turning brazil-wood test paper yellow belongs not only to hydrofluoric acid, but likewise to a few other acids, namely, phosphoric and oxalic acids, and may serve to distinguish them from sulphuric, nitric, arsenic, and boracic acids.

* According to Smithson, hydrofluoric acid is disengaged from fluor-spar and topaz even without the help of microcosmic

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[1] The common mica contains hydrofluoric acid in the proportions of from 0·56, like that of Utö in Sweden, according to Rose; to 8·53, like that of Zinawald in Bohemia, according to Gmelin; the first contains, according to the same authorities, 1·39, the second, 0·83 of water.—Ed.

salt by heating it before the blow-pipe upon a piece of platinum foil. In order to recognise the disengagement of hydrofluoric acid it is necessary slightly to fold the platinum foil so as to form a gutter or cylinder, and push about half of it in a glass tube, open at both ends. Whilst blowing, the glass tube must be held in a somewhat slanting position, in order to permit the hydrofluoric acid which is disengaged to traverse it, and by which it is corroded and rendered opaque. This process may also be resorted to for other combinations which contain a metallic fluoride. According to Smithson the experiment may be modified in the following manner:—The tube is to be fixed into a cork by means of a metallic wire, and the substance under examination being attached to the extremity of a platinum wire by means of a little clay, this platinum is stuck also in the cork in such a way that the substance under trial be just opposite to the inferior aperture of the tube, and that by blowing upon it the flame be driven into the tube.

* When a compound contains only a small quantity of metallic fluoride, but mixed at the same time with a little water, the presence of fluorine may often be ascertained in the following manner:—The combination is to be introduced into a thickish glass tube, closed at one end, and in the open part of which a strip of moist brazil-wood test paper is placed. Upon submitting the tube to the action of the heat of the blow-pipe, fluoride of silicium (fluosilicic acid) is disengaged, if the compound contained silica, and a ring of silica (silicic acid) is deposited at a short distance from the heated point, whilst the extremity of the brazil-wood test paper in the tube becomes yellow. But if the combination contains no water, these phenomena do not take place, even though the compound might contain a large quantity of metallic fluoride.

* A great number of metallic fluorides are not decomposed by exposure to a red heat in contact with the air. There are several however which, like some chlorides, undergo partial decomposition during the operation. This is owing to the moisture of the air. A little hydrofluoric acid is disengaged, and a small quantity of the metal is transformed into oxyde.

* The simple combinations of fluorine form, when they unite together, double compounds, which often have properties quite different from their constituent principles, owing to which circumstance were the operator to examine them superficially, he might altogether overlook the presence of fluorine.

HYDROFLUOSILICIC ACID AND METALLIC SILICOFLUORIDES.

(*Acide Siliciſluorhydrique* and *Siliciſluorures Métalliques.*)

The most important of the combinations which fluorides form by uniting with each other, are those of fluoride of silicium with other metallic fluorides. Fluoride of silicium in the pure state is a colourless gas, which has a suffocating acid smell, and which emits fumes in contact with the air. It does not attack glass. When, however, the latter is damp, it becomes covered with a very adhesive coating of silicic acid (silica). It is absorbed by the hydrofluorides, but not by the dry metallic oxydes. It is largely soluble in water, but is thereby partially decomposed; silicic acid is deposited in the gelatinous state, and a combination of fluoride of silicium and of hydrofluoric acid is dissolved (*hydrofluosilicic acid*). If only a small quantity of water has been employed, the whole mass is converted by the liberated silicic acid into a semi-transparent mass. Hydrofluosilicic acid has an acid taste, and is volatilised at the same temperature as water.

* When this acid is evaporated, it undergoes decomposition, and hydrofluoric acid remains. Hydrofluosilicic acid does not corrode glass, yet when it is evaporated in glass vessels they are corroded by the hydrofluoric acid liberated during the operation. If a drop of hydrofluosilicic acid be evaporated upon a piece of glass, a stain is produced thereon, which cannot be removed by washing.

* Hydrofluosilicic acid combines with the basic metallic oxydes, and produces double fluorides (METALLIC SILICOFLUORIDES). In order to obtain these silicofluorides, it is necessary to add an excess of hydrofluosilicic acid to the base, or at any rate to use as much of it as is necessary to saturate the base. When the base is in excess, the metallic silicofluoride produced

is decomposed, and silica separates in flakes[1]. The solutions of the metallic silicofluorides, the metals of which form alkalies, are, according to Berzelius, the only ones from which the alkalies can separate pure silicic acid, and which consequently are thus transformed into pure metallic fluorides. Ebullition, however, is necessary to effect this decomposition. When a CARBONATE OF ALKALI has been employed to produce it, carbonic acid is disengaged with effervescence whilst the liquor is heated: the silicic acid is dissolved by the excess of carbonate of alkali, and separates on cooling, under the form of an opaline jelly. The solutions of alkalies being poured in those of the metallic silicofluorides, the metals of which form alkaline earths, separate silicic acid mixed with the fluoride of the metal of the alkaline earth which is not decomposed by the alkalies, whilst the fluoride of the alkaline metal formed remains in solution. The alkalies being poured in the metallic silicofluoride, the metals of which produce earths and metallic oxydes, properly so called, separate silicic acid in combination with the earth, or with the metallic oxyde, whilst all the fluorine of the metallic silicofluoride forms a metallic fluoride with the metal of the alkali. If the metallic oxyde which has separated be soluble in ammonia, it does not prevent this re-agent from separating the silicic acid, not alone, but in combination with a certain quantity of the oxyde.

* Among the metallic silicofluorides, those of potassium, of sodium, and of barium, are very sparingly soluble in water; wherefore *hydrofluosilicic acid* may be employed to detect potash, the more especially as the properties of silicofluoride of potassium are remarkable (page 4). *Hydrofluosilicic acid* serves also to detect baryta, or rather to distinguish it from strontia, and from lime (pages 24, 30, 35). The other metallic silicofluorides, even those of lead and of silver, are very soluble in water.

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[1] When an excess of base is employed, the silicofluoride produced is thereby decomposed, in consequence of which silicic acid separates and a metallic fluoride is formed; but when the quantity of base is just sufficient to saturate the hydrofluosilicic acid, the result is a double compound, which consists of a metallic fluoride, combined with a quantity of fluoride of silicium, which, according to Berzelius, contains twice as much fluorine as the metallic fluoride does.—ED.

* When concentrated SULPHURIC ACID is poured upon metallic silicofluorides, most of them are promptly decomposed, fluoride of silicium is disengaged under the gaseous form, and it is only when the liquor is heated that liquid hydrofluosilicic acid is produced, which powerfully attracts the moisture of the air. The silicofluorides of calcium and of barium are decomposed by *sulphuric* acid only when they are heated in contact with it above 212° Fahr. If these decompositions are produced in glass vessels they are powerfully corroded during the heating of the liquor. The rationale of this reaction has been explained before. If platinum vessels be employed, the plate of glass with which they have been covered is attacked exactly as is the case when metallic fluorides are decomposed by sulphuric acid.

* Hydrofluosilicic acid is only partly disengaged from the metallic silver fluorides by NITRIC and by MURIATIC acids, exactly in the same manner as these acids are only incompletely separated from the metallic nitrates and chlorides by hydrofluosilicic acid. But when hydrofluosilicic acid forms with the bases of these salts compounds which are insoluble, or sparingly soluble, the separation is almost completely effected in the humid way; thus, for example, if hydrofluosilicic acid be poured in the solutions of all the salts of potash, the potash is almost completely separated in the state of silicofluoride of potassium.

* The metallic silicofluorides are decomposed by exposure to a red heat, and are thereby converted into metallic fluorides, fluoride of silicium being at the same time disengaged in the state of gas. The decomposition may be completely effected in distilling vessels, but a protracted heat is necessary to expel the whole of the fluoride of silicium. The decomposition begins sooner in open vessels, but then the metallic fluoride which remains after calcining is ordinarily contaminated by silicic acid, because the fluoride of silicium is decomposed during its volatilisation by the moisture of the air, and often also by the water of crystallisation, when the compound contains any, the consequence being a deposit of silicic acid. The fluoride of silicium may also be decomposed by the water resulting from

the combustion of the alcohol of the spirit-lamp, when the calcining is effected by it in an open platinum crucible. The silicic acid which is liberated in these cases is generally dissolved by the metallic fluoride during fusion, but by dissolving the latter in water the silicic acid is left undissolved. When the metallic silicofluorides which contain water of crystallisation are heated in glass vessels, up to a temperature at which the fluoride of silicium begins to volatilise, a white sublimate of hydrofluosilicic acid is obtained. If this sublimate be examined with a microscope, it is observed that it is composed of limpid drops, which by applying heat may be driven from place to place, but which leave a residuum of silicic acid, if the air finds access in the apparatus.

HYDROFLUOBORICIC ACID AND METALLIC BOROFLUORIDES.

(*Acide Borofluorhydrique* and *Borofluorures Métalliques.*)

Fluoride of boron produces compounds which are similar to those which *fluoride of silicium* forms with the *metallic fluorides*. In the pure state, fluoride of boron is a colourless gas, which emits in the air fumes which are denser than those produced by fluoride of silicium, and which does not attack glass like the latter[1]. It is dissolved in large quantity by water, and with disengagement of heat; whilst the gas is thus dissolving, a white powder is deposited, which is boracic acid, and after cooling, crystals of the same acid are formed in the liquor. The solution is very acid, and contains a combination of fluoride of boron, and of hydrofluoric acid (*hydrofluoboric acid*). If this solution be evaporated before the boracic acid produced by the decomposition of the water has separated, the boracic acid and the hydrofluoric acid unite and reproduce fluoride of boron, when the liquor has reached a certain degree of concentration.

* Hydrofluoboric acid combines with the basic metallic oxydes, and thus forms double compounds of fluorine (*metallic borofluorides*). Most of these compounds are soluble in water. The

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[1] Fluoride of silicium does not attack glass, except when dissolved in water and evaporated, because hydrofluoric acid is liberated during the operation.—Ed

least soluble of them appears to be the borofluoride of potassium, which in every respect has the greatest analogy with the silicofluoride of potassium. A few borofluorides seem not to be decomposed by the salifiable bases, as the reverse is the case with the silicofluorides. Thus *ammonia*, for example, even with the help of heat, does not dissolve borofluoride of potassium in larger quantity than water; and the salt crystallises in a hot ammoniacal solution, as in a hot aqueous one. By this character it may be distinguished from silicofluoride of potassium, since silicic acid is separated from the latter by ammonia. A few borofluorides appear not to be decomposed by boiling with solutions of *carbonate of potash* or *of soda*, or of pure *potash*; at any rate, when borofluoride of potassium is treated by these re-agents, no carbonic acid is disengaged, and as the liquor is gradually cooling the salt separates unaltered therefrom. Other metallic borofluorides, however, are decomposed by the addition of an excess of base, and are converted into metallic fluorides and borates.

* The metallic borofluorides are decomposed by concentrated SULPHURIC ACID, like the metallic silicofluorides, but more difficultly, more slowly, and only with the help of heat. Fluoride of boron gas is first evolved, and then hydrofluoboric and hydrofluoric acids are ordinarily formed, and ultimately there remains a sulphate. If the decomposition has taken place in platinum vessels, the plate of glass with which they may have been covered will be found corroded, as is the case when the simple metallic fluorides are decomposed by sulphuric acid.

* When the metallic borofluorides are exposed to a red heat, the result is a decomposition similar to that which the metallic silicofluorides undergo under the same treatment, but which takes place with more difficulty; fluoride of boron gas is disengaged, which when the metallic borofluoride is not anhydrous, or when the ignition is performed in a small glass retort, is deposited in small drops exactly resembling a sublimate, and a metallic fluoride remains. When the metallic borofluorides are ignited in a platinum crucible, the rim of the cover is coated all

round with fused boracic acid, which the moisture of the air or the water produced by the combination of the alcohol has precipitated from the fluoride of boron gas. When the heat is not very strong, or protracted, the borofluorides are only incompletely decomposed.

* Besides fluoride of silicium and of boron there are still several combinations of fluorine with substances the oxydes of which play the part of acids, which form double compounds with basic metallic fluorides. These compounds when ignited or treated by sulphuric acid, deport themselves in a manner which differs from the behaviour of the borofluorides and silicofluorides under the same treatment. In such cases, no gaseous combination or fluorine is evolved, but when *sulphuric acid* is employed scarcely anything else is disengaged than hydrofluoric acid.

* Hydrofluoric acid is distinguished from all other acids, because it strongly attacks glass, a characteristic property which precludes its being confounded with any other; and it is very easy to recognise the combinations of fluorine in the solid state, because when treated by *sulphuric acid,* as has been indicated above, they corrode glass, which characteristic property distinguishes them from all other substances.

5. HYDROSULPHURIC ACID, SH.

[SULPHURETTED HYDROGEN.]

(*Acide Sulfydrique.*)

* HYDROSULPHURIC ACID, in the pure state, is a colourless gas, which, submitted to a strong pressure and to a low temperature, may be condensed into a colourless and very fluid liquid. Hydrosulphuric acid has a peculiar and disagreeable odour, similar to that of rotten eggs. A very small quantity of this gas is sufficient to communicate its repulsive odour to a large mass of other inodorous gases, so that by the smell alone, the minutest traces of it can be recognised.

* When sulphuretted hydrogen is inflamed in the air, it burns with a blue flame, and sulphurous acid gas is disengaged. It may be inflamed with a burning match. If it be mixed with

oxygen or with atmospheric air and then inflamed, it detonates with extreme violence. In the dry state it is not decomposed by oxygen gas, nor by atmospheric air; but when damp, or when dissolved in water, it is decomposed by these two gases. SULPHUROUS ACID GAS has no action upon it when both gases are dry, but if put in contact with water they decompose each other, water being at the same time formed and sulphur liberated.

* Sulphuretted hydrogen gas is slightly absorbed by concentrated SULPHURIC ACID, a small quantity of sulphurous acid is formed during the operation, and sulphur is liberated. Dilute *sulphuric acid* has no action upon sulphuretted hydrogen. It is decomposed by CHLORINE, and converted into muriatic acid, sulphur being at the same time deposited. BROMINE and IODINE, in the gaseous state, produce the same effect. It is likewise decomposed, and with violence, by fuming NITRIC ACID, sulphur being at the same time liberated.

* Pure sulphuretted hydrogen is entirely absorbed by a solution of pure POTASH; but if it contains hydrogen gas the absorption is not complete. If it contains carbonic acid it renders LIME-WATER turbid as it passes through it.

* Sulphuretted hydrogen is completely absorbed by water, but not in very large quantity, water absorbing only two or three times its own bulk of this gas. The solution is colourless, and has the same disagreeable odour as the gas. The solution reddens litmus paper, but not strongly. When the solution is kept perfectly out of contact of the air it does not undergo decomposition; but exposed to its contact it becomes decomposed in a short time, its hydrogen uniting with the oxygen of the air, and sulphur being liberated. Whilst this reaction is taking place the solution at first becomes milky and gradually loses its odour, and the liberated sulphur is slowly deposited, in which case it has always a white, instead of a yellow colour. Sulphuretted hydrogen may be expelled from its aqueous solution by boiling, though it is difficult to render water inodorous by this means, at least in a short time.

* The aqueous solution of sulphuretted hydrogen is decomposed by almost all the substances by which the gas can be decomposed. The aqueous solution of CHLORINE and, next to it, of BROMINE and IODINE is the most energetic in this respect; whilst this reaction is produced there is always a separation of sulphur and formation of hydrochloric, hydrobromic, and hydriodic acids. The aqueous solution of sulphuretted hydrogen is also easily decomposed by SULPHUROUS ACID; but NITRIC ACID is not so effective in this respect, on account of the state of dilution in which the sulphuretted hydrogen is.

* Sulphuretted hydrogen, by combining with the metallic oxydes, forms METALLIC SULPHURETS. There are but few metallic oxydes, which are not thus converted into metallic sulphurets; of these we shall speak further on.

* The combinations of sulphur with the metals, the oxydes of which form alkalies, are soluble in water. The metals of alkalies combine with sulphur in several proportions, and the compounds resulting therefrom are yellowish-white or brown, when perfectly pure. They all absorb moisture from the air, and resolve into a yellow liquid. They may, in some cases, be obtained in crystals, in which case they contain water of crystallisation. Their aqueous solution renders red litmus paper blue, without exception. The aqueous solution of the sulphurets of the metals of alkalies which contain the minimum of sulphur forms a colourless liquid, which, however, turns yellow by exposure, and, in fact, assumes the same colour as the solutions of the sulphurets of metals of alkalies, which contain more sulphur. The colourless solutions of these sulphurets of metals of alkalies, when concentrated, may dissolve and absorb pulverised sulphur, especially with the help of heat, by which means they assume a yellow colour, and are rendered similar to the solutions of the metallic sulphurets of alkalies, which contain a larger proportion of sulphur.

* The solutions of these metallic sulphurets are decomposed by almost all acids, even by the weakest, and always with disengagement of sulphuretted hydrogen. The metal, when an

oxacid has been employed, is converted into an oxyde, and combines with that oxacid. When the decomposition is effected by means of a hydracid, the metal unites with the radical of that hydracid. Even nitric acid decomposes the solutions of the sulphurets of metals of alkalies with disengagement of sulphuretted hydrogen. If the metallic sulphuret of alkali is one with the minimum of sulphur, its solution, strictly speaking, should not be rendered turbid when decomposed by an acid; yet it always becomes more or less milky, or at least opaline, owing to a liberation of sulphur, because it is impossible to obtain a solution free from all excess of sulphur. When the alkaline sulphurets contain a larger proportion of sulphur, the decomposition of their solution by means of an acid is always accompanied by the formation of a white precipitate, produced by a liberation of sulphur, and this precipitate is always so much the more abundant as the compound contained more sulphur; even the carbonic acid of the air is sufficient to effect this decomposition, wherefore the alkaline sulphurets, both in the solid state and in solution, exhale a feeble odour of sulphuretted hydrogen.

* When the solutions of the alkaline sulphurets, containing much sulphur, are decomposed by means of an acid, especially by pretty strong muriatic acid, taking care to pour the solution drop by drop in the acid and to stir the mixture, sulphuretted hydrogen is always disengaged, but it then often happens that, instead of a precipitate of sulphur, an oleaginous body is formed which falls to the bottom of the vessel, and which is persulphuret of hydrogen[1]. This substance, in course of time, becomes thicker, sulphuretted hydrogen being at the same time disengaged, after which it no longer exhales the odour of sulphuretted hydrogen, but one which is more disagreeable still. After the lapse of a

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[1] To obtain the persulphuret of hydrogen as mentioned, it is necessary that both liquors be not too concentrated, nor yet too dilute, that they be lukewarm, and that they be diligently stirred whilst being mixed; the experiment succeeds better with solution of sulphuret of potassium (liver of sulphur) poured in muriatic acid; persulphuret of hydrogen undergoes gradually spontaneous decomposition.—Ed.

longer time it becomes entirely solid by exposure, and it is then found to consist of almost pure sulphur. This substance cannot always be obtained; a very small quantity of it is always mixed with the sulphur which has been precipitated from the solutions of metallic sulphurets of alkalies by means of an acid, and it is probably owing to its presence that the white colour of the precipitate is due.

* If the alkaline sulphuret contains any carbonate of alkali, which is the case, for example, with the compound known under the name of liver of sulphur, carbonic acid gas is disengaged along with sulphuretted hydrogen, when the decomposition is effected by means of an acid poured in excess.

* By exposure to the air, the solutions of the metallic sulphurets of alkalies undergo a decomposition, which is due not only to the carbonic acid contained in the air, but also to the oxygen of the atmosphere, by which they are converted into hyposulphites of alkalies. If it be a lower sulphuret, the half of the alkali which is thus formed, is sufficient to saturate the hyposulphurous acid produced, the other half remaining in the solution either in a pure state or in the state of carbonate.

* The combinations of sulphur with the metals the oxydes of which form alkaline earths, have much analogy with the metallic sulphurets of alkalies, both with respect to their behaviour towards re-agents, and with their other properties, though they are less soluble in water than the latter. Of all these metallic sulphurets, that of calcium is the least soluble, even when in the lower state of sulphuration. Sulphurets of barium and of strontium are much more soluble. These metallic sulphurets may combine with water of crystallisation.

* The earths and a few of the metallic oxydes, properly so called, are only very difficultly converted into metallic sulphurets. When hydrosulphuret of ammonia is poured into the neutral solutions of their oxysalts, they are generally decomposed in such a way that the ammonia precipitates the earth or the metallic oxyde, whilst sulphuretted hydrogen is set free. Such is the case with the neutral solutions of the salts of alumina (page 46),

of glucina (page 49), of thorina (page 51), of yttria (page 53), of protoxyde of cerium (page 55), of zircon (page 59), and probably also of the salts of chrome (page 198). Sulphuretted hydrogen produces no change in the neutral solutions of these salts.

* Most of the combinations of sulphur with the metals, properly so called, are totally insoluble in water, and in solutions of salts; wherefore, in qualitative and in quantitative analysis, sulphuretted hydrogen gas and hydrosulphuret of ammonia are more particularly employed to precipitate the various metallic oxydes from their solution in the state of metallic sulphurets; for, in most cases, these re-agents determine a complete precipitation of even the slightest traces of the metallic oxydes held in solution. The nature of the precipitates so obtained is often also more easily and certainly recognized than that of the precipitates determined by other re-agents, because they often have a characteristic colour; wherefore sulphuretted hydrogen and hydrosulphuret of ammonia are the most important of all re-agents employed in chemical analysis.

* The composition of the metallic sulphurets precipitated by sulphuretted hydrogen or hydrosulphuret of ammonia is entirely similar to that of the metallic sulphurets found in nature, from which they differ only in their external appearance. These metallic sulphurets behave variously towards re-agents, but with *aqua regia* and with nitric acid their reactions are nearly uniform.

* When, after being pulverised, they are boiled for a long time in AQUA REGIA they become oxydised, but then the metal is always completely oxydised long before the sulphur with which it was combined. The oxydised metal dissolves in the acid, except it be such an oxyde which forms with the muriatic or with the sulphuric acid produced, an insoluble or sparingly soluble compound, as is the case, for example, with silver and with lead. The sulphur takes a longer time to become oxydised; so that after the metallic sulphuret has been completely decomposed, pure sulphur is still left. The sulphur thus liberated is generally of a grey colour, because

it is as yet mixed with some undecomposed metallic sulphuret; but by a protracted ebullition or digestion it becomes yellow. The sulphur thus separated may be collected on a filter, and heated upon a strip of platinum foil, in order to ascertain whether it is actually pure, in which case it should burn with a blue flame, exhale the odour of sulphurous acid, and leave no residuum, or at any rate, an insignificant one. The filtered liquor is a solution of the metal, and contains sulphuric acid; for a portion of the sulphur is always converted into sulphuric acid by the excess of aqua regia employed, but never into a lower degree of oxydisation. The presence of sulphuric acid in the filtered liquid may be readily ascertained by pouring therein a solution of a barytic salt. In order completely to oxydise the sulphur of the metallic sulphuret, it is ordinarily necessary to continue the digestion in aqua regia for a very long time, and to renew it (the aqua regia) several times.

* NITRIC ACID acts upon metallic sulphurets nearly like *aqua regia,* only when sulphurets are treated by hot nitric acid; red fumes of nitrous acid are evolved, and a longer digestion is required to give to the sulphur separated its characteristic yellow colour, than when *aqua regia* is employed. The liquor filtered from the sulphur contains sulphuric acid also. The metallic oxyde is completely dissolved, provided it is one which is soluble in nitric acid, and which does not form an insoluble compound with the sulphuric acid produced. Wherefore, when sulphuret of antimony or of tin is digested with nitric acid, sulphur remains mixed with oxyde of antimony and peroxyde of tin; in the same way, after digesting sulphuret of lead in nitric acid, the sulphur which is liberated contains sulphate of lead, whilst another portion of the oxyde of lead remains dissolved in the state of nitrate of lead. *Sulphuret of mercury* (cinnabar) is almost the only metallic sulphuret which is not decomposed by digestion in *nitric acid;* but if *aqua regia* be employed instead, it is then decomposed in the manner above said.

* Fuming NITRIC ACID acts much more violently upon the

metallic sulphurets than *aqua regia* and ordinary *nitric acid.* When it is poured upon a dry metallic sulphuret, reduced to very fine powder, a disengagement of light is ordinarily manifested, and usually not only the metal, but the sulphur also, is completely oxydised, so that the whole of the sulphuret is converted into a sulphate, which in general dissolves completely in the water which is subsequently added.

* The metallic sulphurets which are insoluble in water do not all behave in this manner towards MURIATIC ACID. Reduced to a state of extreme division, most of them disengage sulphuretted hydrogen when treated by hot *muriatic acid;* which is principally the case with those the metals of which easily decompose water with the help of a dilute acid, such as the *persulphurets of iron* and of *manganese:* it is more difficult to decompose *sulphuret of zinc* in this way, and *sulphurets of nickel* and of *cobalt* still more so; they may even be said to be hardly decomposable in this way. But even the metallic sulphurets, the metals of which thus decompose water with the help of an acid only with much difficulty, or which cannot decompose it at all, often undergoes a complete decomposition under disengagement of sulphuretted hydrogen, when, after having been finely pulverised, they are heated with concentrated muriatic acid. Such is the case with *sulphurets of antimony,* of *lead,* of *bismuth,* of *cadmium,* and of *tin.* In such cases, if the metallic sulphuret contains precisely as much sulphur as is necessary to form sulphuretted hydrogen with the hydrogen of the decomposed muriatic acid, no sulphur is deposited, and the decomposition is completely effected when the metallic chloride is not insoluble; which is the case with the degrees of sulphuration of iron and of antimony which correspond to the lowest degrees of oxydisation of these metals. But if the metallic sulphurets contain more sulphur than is necessary to form sulphuretted hydrogen with the hydrogen of the decomposed muriatic acid, then the excess of sulphur is liberated, and sulphuretted hydrogen gas is disengaged. It is, however, difficult then to obtain the precipitated sulphur with its characteristic pure yellow colour. The higher degrees of

sulphuration of iron and of antimony are examples of this reaction.

* The metallic sulphurets which are insoluble in water behave differently with highly diluted muriatic acid. Several of them are easily dissolved by this acid, and likewise in other diluted acids, whilst others, when the liquor contains sulphuretted hydrogen in excess, are totally insoluble in muriatic and other dilute acids, even though *concentrated muriatic acid* may easily dissolve them. Hence the metallic sulphurets which are formed in the metallic solutions which are precipitated by sulphuretted hydrogen may be divided into two pretty distinct classes, namely:—

1st. Metallic sulphurets which are precipitated by an excess of sulphuretted hydrogen from their alkaline, and sometimes from their neutral, but not from their acid metallic solutions.

2nd. Metallic sulphurets which are precipitated from their dilute acid metallic solutions by an excess of sulphuretted hydrogen. The metallic oxydes themselves may be divided into these two classes also[1]. In treating formerly of the deportment of the various metallic oxydes towards re-agents, I have always taken care to notice the reaction which sulphuretted hydrogen determines in the acid and the neutral solutions of the bases. I shall, however, give further on, a summary table of the various metallic oxydes, arranged according as they produce similar or different reactions with sulphuretted hydrogen, and with hydrosulphuret of ammonia.

METALLIC SULPHURETS OF THE FIRST CLASS.

* The metallic sulphurets of the first class are therefore those which are precipitated by sulphuretted hydrogen from the alkaline solutions of the metallic oxydes of the first class; they are produced also when *hydrosulphuret of ammonia* is poured in the neutral solutions of these metallic oxydes. Therefore, in order to precipitate a metallic oxyde of the first class in the state of

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[1] See the synoptic table at page 471.

metallic sulphuret, if the solution be acid, it must be rendered neutral or alkaline by adding an alkali, especially ammonia; an excess of alkali does not prevent the precipitation of the metallic sulphuret; after which *hydrosulphuret of ammonia* is poured in. Even when the metallic oxyde is precipitated by the excess of alkali, it is nevertheless easily and completely converted into metallic sulphuret as soon as a sufficient quantity of hydrosulphuret of ammonia is added. In such cases a pretty large excess of hydrosulphuret of ammonia may be employed, without fear of dissolving the metallic sulphuret produced. Most of the metallic oxydes of the first class are not precipitated by sulphuretted hydrogen from their neutral solutions, because at the same time as the metallic sulphuret is formed the acid with which the metallic oxyde was combined is set at liberty, and dissolves the sulphuret as fast as it is produced. This case, however, occurs only when the metallic oxyde is united to a strong (inorganic) acid, such as sulphuric, muriatic, nitric acids, &c. Some metallic oxydes of this class, the sulphurets of which are difficultly soluble in acids, are partially precipitated in the state of metallic sulphurets from their neutral solutions by sulphuretted hydrogen; but the precipitation ceases as soon as the formation of the sulphuret has liberated a sufficient quantity of acid, which then prevents the formation of any more sulphuret. The solutions of the neutral salts of zinc are in that predicament.

* When, on the contrary, the metallic oxydes of this class are united with very weak organic acids, they may be partially, or even at times totally, precipitated from the solutions, in the state of metallic sulphurets, by means of sulphuretted hydrogen. Thus, for example, peroxyde of tin is completely precipitated when combined with acetic acid, and even when a great excess of acetic acid is added to the solution of the neutral acetate of tin, the whole of the peroxyde of tin may be precipitated in the state of persulphuret of tin, by means of sulphuretted hydrogen. If, on the contrary, the solution contains even a small quantity of a strong inorganic acid, the separation of the peroxyde of tin in the state of persulphuret of tin is not completely effected.

Oxyde of cobalt and of *nickel* are likewise wholly precipitated from their neutral solutions in *acetic acid* by sulphuretted hydrogen, in the state of sulphurets of cobalt, or of nickel; but if acetic acid be added to the solutions of their neutral acetates, no precipitate takes place, and the whole of the oxyde remains dissolved after treatment by sulphuretted hydrogen. A solution of neutral *acetate of protoxyde of manganese* does not at first yield any precipitate by sulphuretted hydrogen, but after some time sulphuret of manganese is separated. If, however, free *acetic acid* be added to the solution, no sulphuret of manganese is precipitated. Sulphuretted hydrogen precipitates iron in the state of black sulphuret of iron from a solution of neutral acetate of peroxyde of iron, but if the solution contains any free acetic acid a yellowish-white precipitate of sulphur only is obtained.

METALLIC SULPHURETS OF THE SECOND CLASS.

* The metallic sulphurets of the second class are combinations of sulphur with the metals of the oxydes of the second class, that is to say, of the oxydes which are precipitated from their acid solutions by sulphuretted hydrogen. When a metallic oxyde of the second class is precipitated from its acid solution in the state of metallic sulphuret, by sulphuretted hydrogen, the precipitated sulphuret which has been first formed, can seldom be distinguished from that which is formed at a later period, when the solution is nearly saturated by the sulphuretted hydrogen, because in most cases the metallic sulphuret first precipitated does not combine with the metallic oxyde as yet undecomposed. Protoxyde, protochloride, protobromide, and protofluoride of mercury, are exceptions to this rule. When a small quantity of sulphuretted hydrogen gas is passed through these solutions, a white precipitate is formed. It is true that at the surface of the liquid, just where the bubbles of sulphuretted hydrogen gas burst, a black precipitate of sulphuret of mercury is observed, but this precipitate becomes quite white when stirred about in the liquid, provided the latter contain as yet much of the salt of mercury undecomposed. This white precipitate remains for a

long time suspended in the liquor, and it consists of an insoluble combination of the protosulphuret of mercury produced, mixed with a portion of the protosalt of mercury, (*sel mercurique*) as yet undecomposed. If sulphuretted hydrogen continues to be passed a little longer through the liquor, a mixture of a black and of a white precipitate is obtained by stirring the liquor; but if an excess of sulphuretted hydrogen is passed through the solution, the precipitate obtained is altogether black and heavy, and it then consists of pure protosulphuret of mercury, (*sulfure mercurique, cinnabar.*)

* Among the metallic oxydes of the second class, those which act as powerful bases are more easily and more rapidly precipitated from their solutions in the state of metallic sulphurets, by sulphuretted hydrogen, than those which act as acids. The latter are completely precipitated from their solutions only when after having supersaturated it with sulphuretted hydrogen, they are left at rest until they have almost entirely lost the odour of sulphuretted hydrogen; the precipitation is accelerated by applying heat. The precipitation of the metallic sulphuret is likewise promoted by the addition of a dilute acid to the liquor. The solutions of peroxyde of tin, the different egrees of oxydisation of antimony, of arsenic, &c., belong to this order.

* A great portion of the metallic oxydes of the second class are completely precipitated from their neutral or alkaline solutions in the state of metallic sulphurets, by hydrosulphuret of ammonia, and most of these sulphurets do not dissolve in an excess of this re-agent, even though the oxyde be very soluble in ammonia. Thus the metallic oxydes are completely precipitated in the state of metallic sulphurets, from the ammoniacal solutions of salts of silver, and of protoxyde of copper, by hydrosulphuret of ammonia.

* Other metallic oxydes of the second class, on the contrary, especially those which act more like acids than like bases, cannot be completely precipitated from their neutral or alkaline solutions by hydrosulphuret of ammonia, because the metallic sulphurets which are thus formed are more or less soluble in an

excess of the re-agent. In this respect the metallic sulphurets of the second class may again be subdivided into two sections, namely:—

Metallic sulphurets which are soluble in an excess of hydrosulphuret of ammonia.

Metallic sulphurets which are not soluble in an excess of hydrosulphuret of ammonia.

These two subdivisions are equally applicable to the metallic oxydes of the second class. When treating of each combination of a metallic oxyde with sulphur, I have already indicated the behaviour of such combinations towards an excess of hydrosulphuret of ammonia; considering, however, that it is of the highest importance in chemical analysis, to know these reactions in a thoroughly exact manner, I shall hereafter summarily recapitulate them.

* The solubility of certain metallic sulphurets in hydrosulphuret of ammonia, depends upon the affinity of these two bodies for each other, similar to that which oxacids have for the oxybases, or fluoride of silicium, fluoride of boron, and some other compounds of fluorine for the basic metallic fluorides.

The composition of the compounds which the combinations of sulphur with the metals, the oxydes of which play the part of acids by uniting with hydrosulphuret of ammonia, or with metals the oxydes of which play the part of bases, has much resemblance with the oxysalts, or with the metallic silicofluorides or borofluorides. We are indebted to Berzelius for this discovery, and they were called by him SULPHOSALTS. The principal sulphosalts are the combinations of sulphur with arsenic, tungsten, molybdenum, vanadium, antimony, tin, and tellurium, which by uniting with the sulphurets of the basic metals produce these saline combinations, a great number of which may be obtained in crystals, and contain water of crystallisation. The sulphosalts which have an alkaline sulphuret, or a sulphuret of alkaline earth for a base, are ordinarily soluble in water, whilst those which contain sulphuret of metals, properly so called, appear generally to be insoluble in that menstruum.

* The most important sulphosalts, at present known, are the following:—

* SULPHARSENIATES.—These contain arseniuretted hydrogen, that is to say, the degree of sulphuration of arsenic, which corresponds by its composition to arsenic acid ($As+S_5$). Their properties, according to Berzelius, are as follow: their colour varies; those which have an alkaline sulphuret for a base are of a lemon-yellow colour in the anhydrous state, and colourless, or simply yellowish, when they contain water of crystallisation. They have a hepatic and extremely disagreeable taste. They are decomposed by dilute muriatic acid, and other acids, when the basic sulphuret which they contain is easily decomposable by acids, in which case sulphuretted hydrogen is disengaged, whilst persulphuret of arsenic is deposited under the form of a yellow precipitate; yet this yellow sulphuret is not completely deposited, unless the liquor be left at rest for a long time, or else by applying heat. If a very dilute solution of a sulpharseniate be decomposed by an acid, no effervescence is produced, and the liquor only exhales the odour of sulphuretted hydrogen. Persulphuret of arsenic is precipitated even when a current of carbonic acid is passed through the solution of these salts.

* The sulpharseniates of the metals of the alkalies, or of the alkaline earths, of glucina, and of yttria, and a few also of those formed by some of the metals, properly so called, are soluble in water, whilst the others are insoluble therein. The solutions of these salts are decomposed by alcohol, a subsalt is precipitated, and a salt which contains double the quantity of sulphuret of arsenic remains in solution. If, by submitting the filtered liquid to distillation, half, or a little more than half, of the alcohol is abstracted, crystalline, yellow, and shining spangles deposit on cooling, which spangles often altogether fill up the space occupied by the liquid, though their quantity in weight is very small. These crystalline spangles melt almost as easily as sulphur. They consist of persulphuret of arsenic, that is to say, that degree of sulphuration of the metal in which there is more sulphur than in that which corresponds to arsenic acid. By continuing the

evaporation, a lower degree of sulphuration, which has a red colour is again separated from the liquor.

* Exposed to dry distillation, the neutral sulpharseniates lose a portion of their sulphur, and become converted into sulpharsenites; the basic sulpharseniates, on the contrary, undergo no alteration. Heated in contact with the air, they are easily decomposed, leaving the base either simply in the state of oxyde, or combined with sulphuric acid; sometimes the residuum contains arsenic acid besides. The solutions of these salts are often decomposed by the metallic oxydes, the result being the formation of an arseniate, which remains dissolved in the liquor, and a subsulpharseniate which is deposited.

* The concentrated solutions of the sulpharseniates may be kept in open vessels tolerably well, but their dilute solutions are decomposed. Yet their decomposition proceeds only slowly, and several months must elapse before it is complete. The liquor becomes turbid, deposits sulphuret of arsenic ($As\,O_5$) and sulphur, and consists then not only of some as yet undecomposed sulpharseniate, but also of some arsenite and hyposulphite, which latter substance, when the decomposition has been completed, is converted into a sulphate.

* SULPHARSENITES.—These salts contain sulphuret of arsenic ($As\,S_3$), that is to say, the degree of sulphuration, the composition of which corresponds to arsenious acid ($As\,O_3$). According to Berzelius, they can be obtained in the neutral state, and in the solid form only in the dry way, because, when their solutions are brought to a certain degree of concentration, they are decomposed, and deposit a brown powder, which is a hyposulpharsenite, whilst a basic sulpharseniate remains in the liquor, yet the decomposition is completed only when the latter salt begins to crystallise. By diluting the liquor with water, or boiling it, the precipitate dissolves, and the sulpharsenite is reproduced. This decomposition likewise takes place by treating with a small quantity of water the salt prepared in the dry way, and also by pouring alcohol in a dilute solution of sulph-

arsenites, whilst the alcohol determines the precipitation of a subsalt, which subsequently undergoes a decomposition, as we have just described, and becomes black after a few moments. When alcohol is poured in the solutions of *basic sulpharsenites*, of *baryta*, of *lime*, and of *ammonia*, the decomposition of the precipitated subsalt does not take place, and is effected only when the solution contains either a neutral salt, or a salt containing an excess of arsenious sulphuret.

* The sulpharsenites which have an alkali for a base are not decomposed by being submitted to dry distillation; the alkaline sulphobase may retain, at a red heat, several times as much arsenious sulphuret as is necessary for its saturation. The other sulpharsenites are decomposed by a dry distillation; some arsenious sulphuret passes over, and at times a subsalt, at other times the sulphobase alone remains.

* The sulpharsenites behave like the sulpharseniates with the metallic oxydes, the acids, and when put in contact with the air; also when exposed to a red heat in contact with the air.

* HYPOSULPHARSENITES.—These salts contain the hypo-arsenious sulphuret (realgar, or red sulphuret of arsenic) $As+S_2$, which is a degree of sulphuration which does not correspond to any degree of oxydisation of the metal. Their colour is red or deep brown. According to Berzelius, the neutral hyposulpharsenites which have been prepared in the dry way are decomposed by water, a black or deep brown sulphuret of arsenic to the minimum of sulphuration is deposited, and a sulpharseniate remains in solution. Most of these salts are insoluble in water. Acids separate some hypo-arsenious sulphuret from them.

* SULPHOMOLYBDATES.—These salts contain the sulphuret of molybdenum, that is to say, the brown sulphuret of molybdenum, the composition of which corresponds to molybdic acid ($Mo+S_3$). Berzelius describes their properties as follows: Those which have alkaline sulphurets and sulphurets of alkaline earths for a base are soluble in water. The solution, when

neutral, has a fine red colour; if it contain an excess of sulphuret of molybdenum, it is brown; but if the sulphobase predominates, it has a yellow or rusty colour. The sulphomolybdates may be obtained in crystals which are brown or of a ruby colour, or of a ruby colour by transmitted light, and of a fine green colour similar to that of the wings (elytra) of certain coleoptera by reflected light. Acids precipitate a brownish-black sulphuret of molybdenum from this solution under disengagement of sulphuretted hydrogen. They are decomposed by a dry distillation, the sulphobase sometimes combining with part of the sulphur of the persulphuret of molybdenum, and when water is subsequently poured upon this higher degree of sulphuration of the base, it dissolves it, and a grey sulphuret of molybdenum remains. At other times, when the base is not susceptible of passing to a higher degree of sulphuration, the sulphur volatilises and the residuum then contains either a combination or else only a a mixture of grey sulphuret of molybdenum with the sulphobase.

* The concentrated neutral solutions of the sulphomolybdates resist pretty well the action of the air, but they are very rapidly decomposed by exposure when they contain an excess either of the sulphobase or of an oxybase. The dilute solutions of the neutral sulphomolybdates gradually acquire a deeper colour by exposure; a portion of the base absorbs oxygen, and is converted into a hyposulphite; whilst at the same time a sulphosalt with excess of persulphuret of molybdenum is formed in the liquor. The latter salt, in course of time, is also decomposed, persulphuret of molybdenum is deposited, the liquor becomes blue, and it then contains the oxybase combined both with the sulphur acids and with molybdic acid. The blue colour of the liquor is due to the presence of molybdate of molybdenum. This decomposition, however, progresses so slowly that, whilst it is going on, the liquor dries up, and the operator is several times obliged to dissolve the salt before it is entirely decomposed.

* HYPERSULPHOMOLYBDATES.—These salts contain a degree of sulphuration of molybdenum, in which twice as much sulphur

is contained as in sulphuret of molybdenum ($Mo+S_4$), and to which no degree of oxydisation of the metal corresponds: all these salts have a deep-yellow or red colour. They rarely crystallise. They are insoluble in water, except those which have an alkaline base, in which case they are sparingly soluble in cold water, but are dissolved by boiling water, from which they are deposited as the liquor cools. The solution has a deep-red colour. The hypersulphomolybdates are decomposed by acids, sulphuretted hydrogen being disengaged, and sulphuret of molybdenum being separated in the shape of flakes of a fine deep-red colour.

* SULPHOTUNGSTATES.—These salts contain persulphuret of tungsten, that is to say, the degree of sulphuration which corresponds to tungstic acid ($W+S_3$). Those which are soluble have a yellow or red colour. Their solutions are very slowly decomposed by exposure, and may be concentrated so as to crystallise when evaporated by a gentle heat in contact with the air. When these solutions remain exposed for a long time to the air, their colour becomes gradually lighter, sulphuret of tungsten and sulphur are deposited, and a tungstate and a sulphate remain in solution. When the liquor contains an excess of base, decomposition takes place very rapidly.

* SULPHOVANADATES.—These salts contain the sulphuret of vanadium corresponding to vanadic acid ($V+S_3$). Those which have an alkaline sulphobase for a base are very soluble; those sulphovanadates of sulphurets of metals which produce alkaline earths are sparingly soluble, and the other sulphovanadates of metallic sulphurets are often insoluble. They have a deep-brown colour; their aqueous solution is brown, and they are precipitated therefrom by alcohol.

* SULPHOVANADITES.—These salts contain the lowest degree of sulphuration of vanadium ($V+S_2$). The sulphovanadites of the alkaline sulphobases are soluble in water; their solution has

a very fine purple colour [nearly as fine as that produced by the solutions of the oxymanganates]. They are obtained by passing a current of sulphuretted hydrogen gas through a solution of vanadite of potash. A very small portion of foreign metallic oxyde is sufficient to impair the beauty of the colour of this solution.

* Sulphotellurites.—These salts contain a sulphuret of tellurium corresponding to tellurous oxyde ($Te+S_2$). They are soluble in water when their base is the sulphuret of a metal of alkali, or of alkaline earth. Their solutions are rapidly decomposed by exposure. These salts can be kept for a long time in the dry state, but the least moisture determines their decomposition, in which case the sulphobase is converted into a hyposulphite, and sulphuret of tellurium is deposited. Most sulphotellurites may be exposed to a red heat in a closed vessel without undergoing decomposition; but those which have a weak base are decomposed by a red heat, the sulphur being expelled from the sulphuret of tellurium, and the liberated tellurium subsequently expels a portion of the sulphur of the sulphobase, and there remains a mass having a metallic lustre, and which consists of a metallic telluride, and of a metallic sulphuret.

* Sulphantimoniates.—These salts contain the sulphuret of antimony corresponding to antimonic acid ($Sb+S_5$), and which is separated under disengagement of sulphuretted hydrogen gas when they are treated by acids. The sulphantimoniates, the base of which is an alkaline sulphobase, are soluble in water, and may be crystallised. The crystals are colourless, or have a feeble-yellowish tinge, and do not yield sulphur by a dry distillation. When submitted to a red heat in closed vessels, and the residuum exposed to the air, it falls into a bulky powder. When the crystals are exposed for a long time to the air, they are gradually decomposed, and become superficially of a reddish-brown colour, due to a separation of sulphuret of antimony.

* HYPOSULPHANTIMONITES.—These salts contain the ordinary sulphuret of antimony at the minimum of sulphuration ($Sb + S_3$). They have not as yet been artificially produced, but are frequently found crystallised in nature, and they form a series of sulphosalts, which, in a technical and scientific point of view, are very important.

* SULPHOSTANNATES.—These salts contain the sulphuret of tin corresponding to the peroxyde of tin ($Sn + S_2$). The sulphostannates, whose sulphobase is a metal of alkali, or of alkaline earth, are soluble in water, from which solution they may be precipitated by alcohol, and then those which have an alkaline base assume an oily consistence. Out of the contact of the air they may be submitted to a red heat without being decomposed.

* The sulphurets of the metals, the oxydes of which play the part of an acid, are not the only combinations of sulphur which produce sulphosalts by combining with the basic metallic sulphurets. Sulphosalts are likewise produced by the combinations of sulphur, principally sulphuretted hydrogen and persulphuret of carbon, with some other bodies.

* Berzelius has given the name of *sulphydrates* (hydrosulphurets) to the combinations which sulphuretted hydrogen forms with the metallic sulphobases[1]. The sulphurets of the metals of alkalies and of alkaline earths are the only ones which can produce sulphosalts by combining with sulphuretted hydrogen. These sulphydrates (hydrosulphurets) are formed by passing a current of sulphuretted hydrogen gas for a long time through solutions of alkalies or of alkaline earths. Hydrosulphuret of ammonia (*sulphydrate ammonique*), which is employed as a re-agent, belongs therefore, when well prepared, to this order of salts. The combinations of sulphuretted hydrogen with the metallic sulphurets of alkalies, may be exposed to a red

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[1] Sulphuretted hydrogen converts all the alkalies, all the earths, and the oxydes of many other metals, into metallic sulphurets, or, which is the same thing, into the bases of sulphosalts.—ED.

heat out of the contact of the air, without being decomposed; but hydrosulphuret of barium and of strontium lose their sulphuretted hydrogen when thus treated. Hydrosulphuret of calcium and magnesium (*sulfhydrate calcique et magnésique*) can be obtained only in solution. The hydrosulphurets have much analogy with the metallic sulphuret which constitutes their base, and resemble it in almost every respect. They cannot be distinguished from each other otherwise than by pouring in their concentrated solution, a neutral solution, also concentrated, of a salt of zinc, or of a protosalt of manganese or of iron: in both cases an insoluble metallic sulphuret is formed; but in the first case this formation is accompanied by a disengagement of sulphuretted hydrogen, which does not take place when the experiment is performed with the solution of a simple metallic sulphuret of alkali. The solutions of hydrosulphurets, properly speaking, are colourless, but by exposure to the air they are very easily decomposed; a portion of the sulphobase absorbs oxygen, and is converted into a hyposulphite, whilst the other portion passes to a higher degree of sulphuration; in effect, the hydrogen of the sulphuretted hydrogen by combining with oxygen forms water, whilst its sulphur combines with the sulphobase. It is owing to this reaction that the colourless solutions of hydrosulphurets turn immediately yellow by the contact of the air, which is especially the case with hydrosulphuret of ammonia.

SULPHOCARBONATES.—These salts are produced by the combinations of sulphuret of carbon ($C + S_2$) with the metallic sulphobases, with which, however, it unites only with difficulty. The salts of this class, the base of which is a metallic sulphuret of alkali, have a yellow colour which is deeper than that of liver of sulphur. Their taste at first is fresh and peppery, followed by a hepatic, disagreeable flavour. They are decomposed in close vessels by a red heat. The sulphocarbonates which have a metallic sulphuret of alkali for a base, at first fuse, and then undergo a decomposition, the result of which is that the metallic sulphobase combines with a larger quantity of sulphur, and carbon is liberated[1]. The sulphocarbonates which contain sulphurets of the alkaline earths, or of metals properly so called, lose their sulphuret of carbon when exposed to a red heat in closed vessels. The dry sulphocarbonates and their concentrated solutions are not much altered by exposure, but their dilute solutions are thereby very rapidly decomposed; they are decomposed by boiling, even out of the contact of the air, the water being decomposed, a carbonate formed, and sulphuretted hydrogen disengaged. The sulphocarbonates which have a metal of alkali or of an alkaline earth for a base are soluble in water; the others are insoluble in this menstruum, but dissolve more or less largely into the solutions of the soluble sulphocarbonates. When a sulphocarbonate, soluble in water, is mixed with muriatic acid, a yellow oleaginous body separates, which is a combination of sulphuret of carbon with sulphuretted hydrogen[2], and which results from the decomposition of the metallic sulphobase; the liquor at first has a yellow milky appearance, and after the lapse of a certain time the oleaginous body settles at the bottom.

* Besides the combinations of sulphur above alluded to, there are several others, which have also the property of forming sulphosalts by uniting with the metallic sulphobases. Several of these salts, however, have either not been obtained, or else have not been well examined, and therefore these properties cannot be treated of here[3]. It may be admitted in general, that an insoluble

metallic sulphuret, which at the moment of its precipitation is easily dissolved by an excess of *hydrosulphuret of ammonia*, is capable of forming a *sulphosalt*, by uniting with a metallic *sulphobase.* This rule has, however, many exceptions. The solubility of a recently-precipitated metallic sulphuret in a solution of potash indicates likewise a capability of forming a sulphosalt by uniting with a metallic sulphobase. Ordinarily, the metallic sulphurets which are soluble in an excess of *hydrosulphuret of ammonia* are likewise soluble in a solution of potash, whilst all the metallic sulphobases are absolutely insoluble in the latter solution, even though the oxydes of their metals are easily soluble therein. When a metallic sulphuret is dissolved in a solution of potash, a portion of the metal becomes oxydised at the expense of the potash, and the metallic acid thus produced combines with the unreduced portion of the potash, so as to form a potash salt, whilst the potassium liberated forms a sulphuret of potassium by uniting with the sulphur whose metal has been acidified, and produces a soluble sulphosalt with the undecomposed portion of the metallic sulphuret. The solution in potash always contains, therefore, besides the sulphosalt which has formed, an oxysalt which, owing to its sparing solubility, often separates from the liquor. If a dilute acid be added to such a solution of a metallic sulphuret in a solution of potash, the metallic sulphuret is reprecipitated, and there is no disengagement of sulphuretted hydrogen. The acid combines then with the potash, and the sulphuret of potassium which had formed becomes converted by the metallic oxyde into a metallic sulphuret and potash.

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[1] If water be poured upon the residuum, it dissolves a metallic sulphuret, which contains three times as much sulphur as the sulphobase, and carbon remains in the form of a black powder.—Ed.

[2] Hydrosulphocarbonic acid (*sulfide carbohydrique*) is soon decomposed: it reddens blue litmus paper, and in the humid way it expels carbonic acid from its combinations with the salifiable bases, for example, from carbonate of potash, with which it forms a sulphocarbonate, soluble in water.—Ed.

[3] The sulphosalts here alluded to are the *sulphophosphates* and *sulphophosphites*, which are as yet almost unknown, the *sulphaurates*, *sulphiridates*, and *sulphoplatinates*, &c., in which the affinity of the electro-negative sulphuret is very weak, and the *sulphoborates*, *sulphosilicates*, *sulphotitanates*, and *sulphotantalates*, which possibly may be obtained in the dry way, but which water immediately converts into oxysalts under disengagement of sulphuretted hydrogen.—Ed.

* A few metallic sulphurets, such as those of arsenic, of antimony, &c., are also soluble in an excess of a solution of carbonate of potash or of soda without carbonic acid being disengaged, and the product is the same as in a solution of pure potash. No carbonic acid is disengaged, because an acid carbonate of alkali is formed. Hyposulphuret of antimony (*sulfide hypantimonieux*), however, dissolves in the solutions of carbonate of potash or of soda only by boiling, and the greatest portion

of the sulphuret of antimony, which has been dissolved by the sulphuret of potassium or of sodium formed during the operation, separates as the liquor cools, on account of its sparing solubility in this sulphuret, unless heat be applied.

* Most of the salts soluble in water, which consist of an alkaline base, and of a metallic acid, susceptible of being converted by sulphuretted hydrogen into a metallic sulphuret insoluble in water, are transformed into sulphosalts, which remain dissolved in the water, when a current of sulphuretted hydrogen is passed through their solutions. If an excess of dilute muriatic acid be added to the solution, the insoluble metallic sulphuret separates, and sulphuretted hydrogen is disengaged.

* The great importance to the chemical analyst of a thorough knowledge of the behaviour of sulphuretted hydrogen and of hydrosulphuret of ammonia towards the solutions of the different metallic oxydes, induces me to give here a summary recapitulation of the reactions which they produce.

CLASS I.

* METALLIC OXYDES WHICH CANNOT BE PRECIPITATED IN THE STATE OF METALLIC SULPHURETS FROM THEIR ACID SOLUTIONS, BUT WHICH CAN BE THUS PRECIPITATED FROM THEIR ALKALINE SOLUTIONS BY SULPHURETTED HYDROGEN GAS; AND WHICH CAN BE THUS PRECIPITATED FROM THEIR NEUTRAL OR FROM THEIR ALKALINE SOLUTIONS BY HYDROSULPHURET OF AMMONIA.

1. Protoxyde of manganese, and also the higher degrees of oxydisation of manganese.
2. Proto and peroxyde of iron.
3. Oxyde of zinc.
4. Oxyde of cobalt.
5. Oxyde of nickel.
6. Proto and peroxyde of uranium[1].

* HYDROSULPHURET OF AMMONIA precipitates also the follow-

ing metallic oxydes from their neutral solutions, NOT in the state of METALLIC SULPHURETS, but in the state of OXYDES[1], under disengagement of sulphuretted hydrogen :—

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[1] *Oxyde of lantanum* is not precipitated from an acid solution by sulphuretted hydrogen, but hydrosulphuret of ammonia precipitates it from such a solution.—ED.

1. Alumina.
2. Glucina.
3. Thorina.
4. Yttria.
5. Protoxyde of cerium.
6. Zirconia.
7. Titanic acid.
8. Oxyde of chromium ?
9. Tantalic acid.

* The solutions of the *pure alkalies* and of the *alkaline earths* are converted into metallic sulphurets by *sulphuretted hydrogen gas,* but the new combination remains dissolved either in the state of *sulphuret* or in that of *hydrosulphuret.* The neutral solutions of the salts produced by the alkalies and the alkaline earths are not altered by either sulphuretted hydrogen or by hydrosulphuret of ammonia.

CLASS II.

* METALLIC OXYDES WHICH CAN BE PRECIPITATED BY SULPHURETTED HYDROGEN, FROM THEIR DILUTE SOLUTIONS RENDERED ACID, IN THE STATE OF METALLIC SULPHURETS.

1st SECTION.

* METALLIC oxydes which can be precipitated in the state of metallic sulphurets, both by SULPHURETTED HYDROGEN, from their dilute solutions rendered acid ; and by HYDROSULPHURET OF AMMONIA, from their neutral or alkaline solutions, *and which are insoluble in an excess of the latter re-agent.*

1. Oxyde of cadmium.
2. Oxyde of lead.
3. Oxyde of bismuth.

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[1] Hydrated oxydes.

4. Suboxyde and protoxyde of copper.
5. Oxyde of silver.
6. Suboxyde and protoxyde of mercury.
7. Oxyde of palladium.
8. Oxyde of rhodium.
9. Oxyde of osmium.

2ND SECTION.

* METALLIC oxydes which can be precipitated in the state of metallic sulphurets, by SULPHURETTED HYDROGEN, from their *dilute solutions rendered acid,* although often a somewhat long lapse of time is requisite for the purpose, but which cannot be completely precipitated from their NEUTRAL OR FROM THEIR ALKALINE SOLUTIONS, by either *sulphuretted hydrogen,* nor by *hydrosulphuret of ammonia,* because the sulphurets of their metals are more or less soluble in an excess of hydrosulphuret of ammonia, but from which latter solution they can always be precipitated in the state of metallic sulphurets, by pouring a dilute acid therein.

1. Sesquioxyde and deutoxyde of platinum.
2. Oxyde of iridium.
3. Oxyde of gold.
4. Protoxyde and peroxyde of tin.
5. Oxyde of antimony, antimonious and antimonic acids.
6. Protoxyde and deutoxyde of molybdenum and molybdic acid.
7. Tungstic acid.
8. Oxyde of vanadium and vanadic acid.
9. Tellurous and telluric acids.
10. Selenious acid.
11. Arsenious and arsenic acids.

* Properly speaking, PROTOXYDE OF TIN belongs to the first section; but as hydrosulphuret of ammonia always contains an excess of sulphur, it is converted by a large excess of this re-agent into persulphuret of tin, soluble in hydrosulphuret of ammonia (page 173).

* TUNGSTIC ACID should not either be placed in the second section, because its solution in hydrosulphuret of ammonia is almost the only one in which it can be precipitated in the state of sulphuret of tungsten by the dilute acids, which precipitate of sulphuret of tungsten is not produced by passing sulphuretted hydrogen through the acid solutions (page 311).

* Neither can VANADIC ACID and OXYDE OF VANADIUM be precipitated in the state of sulphuret of vanadium, from their solution in hydrosulphuret of ammonia, otherwise than by muriatic acid (page 314).

* The acid solutions of the oxydes which are deoxydised by sulphuretted hydrogen, owing to which a precipitation of sulphur is subsequently determined, cannot be included among the number of the oxydes of this class. Such is the case with the acid solutions of *peroxyde of iron, chromic acid, chloric acid, bromic acid, iodic acid,* and *sulphurous acid*[1].

* It is hardly necessary to remark that the solutions of the metallic chlorides, bromides, iodides, and fluorides behave towards sulphuretted hydrogen like their corresponding oxydes.

* Before the BLOW-PIPE, all the sulphurets deport themselves in a characteristic manner. Heated in the flame of the blowpipe upon charcoal, or in a glass tube open at both ends, they all disengage sulphurous acid, the minutest portion of which may be detected by its odour. When heated in an open tube, if a moistened strip of BRAZIL WOOD PAPER be held in the upper part of the tube, the paper is bleached, however small the quantity of sulphurous acid disengaged may be (page 209). This test should never be omitted, especially with substances which contain *sulphuret of antimony*, because the feeble odour of the

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[1] The precipitate produced by sulphuretted hydrogen in the acid solutions of these substances is altogether one of sulphur, the whole of the bases remaining in solution. This deoxydisement is produced by the hydrogen of the sulphuretted hydrogen uniting with the oxygen of the substance in solution to form water, in consequence of which sulphur is deposited as a white or slightly-yellowish powder. In this way *peroxyde of iron* becomes converted into *protoxyde of iron ; chromic acid* into green *oxyde of chromium ; bromic acid* converts the sulphuretted hydrogen into *sulphuric acid*, and itself becomes reduced into *bromine ; iodic acid* is reduced into *iodine*, and *deutoxyde of manganese* becomes *protoxyde of manganese*.—ED.

oxyde of antimony might overpower that of the sulphurous acid then evolved, and render it imperceptible. Often also there is a sublimate of sulphur at the same time, but frequently also no sulphur sublimes, which is often dependent upon the angle at which the tube is held whilst heated. The substances which contain metallic sulphurets behave like the sulphates towards a bead of silicic acid and soda (page 204). If, however, the metal combined with sulphur were such as to impart a colour to this bead, another method may be resorted to to detect in an absolute manner, and by means of the blow-pipe, the presence of sulphur. In such a case the substance is to be fused with soda upon charcoal, and then deposited upon a piece of silver, where it is to be moistened; if it contained a metallic sulphuret, the silver is seen to have become black or deep yellow at the point of contact (page 204).

* When in testing the metallic sulphurets before the *blow-pipe* the object in view is to detect the metal, it is necessary in most cases to expel the sulphur as completely as possible by roasting the sulphuret. To effect this, the operator chooses *thin* plates of the natural metallic sulphuret, because the air has more action upon such plates; and for the same reason, pieces which are in round and thick masses should be avoided. At first they are only heated gently, so as not to fuse them; if, however, they should fuse, it is best at once to take another piece, or to pulverise the fused mass. When the roasting has been continued for some time, some sulphurets can no longer be fused; and in such cases a strong fire may be given, in order to decompose the sulphate which is ordinarily formed during the operation. The roasting may be very well effected upon charcoal.

* It is only after the roasting has been completed that the reactions produced by the fluxes can be advantageously resorted to; but when soda is the flux to be employed for effecting the reduction of the metallic oxyde produced, it is important to expel all the sulphur as much as possible, for without this precaution metallic sulphurets are produced which are not so easily

recognised as the metals themselves, or which, dissolving in the sulphuret of sodium produced, are carried away by the water used for washing.

* The metallic sulphurets are fixed, out of the contact of the air, when the metals of which they consist are not volatile. On the contrary, the volatile metals form metallic sulphurets which are volatile also, though not so volatile as the metals themselves. Such is the case with the sulphurets of mercury, of arsenic, of selenium.

* Exposed to a red heat out of the contact of the air, several of the higher degrees of sulphuration of the metals lose part of their sulphur, and are reduced to a lower degree of sulphuration. It is difficult, however, to expel the excess of sulphur so completely as to obtain these lower degrees of sulphuration in a pure state. Such is the case with the higher degrees of sulphuration of iron, of copper, of tin (*aurum musivum*), and of antimony. Calcined in the air, most sulphurets are converted into basic sulphates. I have indicated above, the deportment of the sulphosalts under the influence of a high temperature.

* The external appearance of the metallic sulphurets is very similar. Some of those found in nature have a metallic lustre, like the metals themselves: others have not this lustre. Those which have been artificially produced in the humid way, very frequently, and notwithstanding the identity of their composition, have quite a different colour from those found native, or which have been prepared in the dry way. For example, sulphuret of antimony, either native or prepared in the dry way, has a black colour and a metallic lustre, whilst the sulphuret of antimony obtained in the humid way is red and without lustre. The native sulphuret of mercury, and that prepared by subliming, are red, whilst the sulphuret of mercury obtained in the humid way is black.

* Many of the sulphurets prepared in the humid way, especially those which are produced by pouring hydrosulphuret of ammonia into neutral or alkaline solutions, absorb the oxygen of the air with an extreme facility, which is not the case with those found

in nature. It is owing to this that sulphuret of iron, which is black at the moment it is precipitated, becomes reddish-brown on the filter; sulphuret of manganese becomes brown, &c.

* Sulphuretted hydrogen is so easily recognised by its odour, that it is scarcely necessary to resort to other means to detect its presence, even in minute quantity. But it may be recognised by the precipitate produced by pouring in its solution one of a metallic oxyde prepared by that of an oxyde of lead. It may also be recognised by the brown colour which it imparts to paper moistened with a solution of oxyde of lead. When the presence of sulphuretted hydrogen is suspected in a gaseous mixture, a paper moistened with solution of basic acetate or nitrate of lead will indicate it. Metallic sulphurets are easily recognised by the blow-pipe.

* The presence of ORGANIC SUBSTANCES interferes less with the action of sulphuretted hydrogen and of hydrosulphuret of ammonia than is the case with the other re-agents; a circumstance which enhances their value, since they can still furnish precise and accurate results where the other re-agents only yield deceptive indications. There are, however, certain organic substances which being dissolved in water may yield, by treatment with sulphuretted hydrogen, precipitates which resemble certain metallic sulphurets prepared in the humid way.

6. HYDROSELENIC ACID, Se + H.

[ACIDE SÉLÉNHYDRIQUE.]

(Seleniuretted Hydrogen.)

* IN the pure state, hydroselenic acid is a colourless gas, having a very disagreeable odour, which perfectly resembles that of sulphuretted hydrogen, but which when present in even the minutest quantity acts in the most violent manner upon the trachea and the organs of respiration. This gas is very easily decomposed by the moist organic substances, to which a red colour is imparted by the reduced selenium. This red colour is not only superficial, but it penetrates their interior, especially when very porous. It seems to be more soluble in water than

sulphuretted hydrogen. The solution is colourless, but by exposure it assumes a reddish tinge, produced by a liberation of selenium; in other respects it has the greatest resemblance with the aqueous solution of sulphuretted hydrogen. It reddens litmus paper, and has a hepatic taste.

* Hydroselenic acid forms with the metallic oxydes compounds which are called METALLIC SELENIURETS. This gas seems to precipitate the various metallic oxydes from their solutions in the same manner as sulphuretted hydrogen does, but the oxydes of iron appear to be precipitated by hydroselenic acid from their neutral solutions, when combined with strong acids.

* The metallic seleniurets have much resemblance with the corresponding sulphurets, with respect to their properties and their deportment towards the re-agents. This analogy extends to those found in nature. They differ from the metallic sulphurets and other substances, principally by the phenomena which they exhibit before the BLOW-PIPE. When heated in the exterior flame they emit a very strong and disgusting odour of decayed horse-radish. This odour is so characteristic, that it is sufficient to betray the least traces of selenium. With the glass of silicic acid and soda they present the same reactions as the metallic sulphurets, though the red or brown colour which they impart to this glass disappears more easily by a prolonged insufflation. When treated by soda upon charcoal in the interior flame of the blow-pipe, and the mass, being thrown upon a piece of silver, is moistened thereon, they leave a black or brown stain exactly like the metallic sulphurets.

* When the metallic seleniurets are heated in a glass tube open at both ends, it is often easy, by holding the tube at a suitable angle, to sublime a portion of the selenium in a state of purity and with a red colour, whilst the other substances are oxydised. Very often, however, in such cases there is a formation of selenious acid, which is deposited in the form of a crystalline net-work in the cooler portion of the tube. If the metallic seleniuret be accompanied by a metallic sulphuret, it

often occurs that by operating, as just said, selenium alone is sublimed, whilst the sulphur escapes in the form of sulphurous acid. Sulphuret of arsenic sublimes sometimes, and closely simulates the appearance of selenium; but when treated with soda upon charcoal, the odour of arsenic is evolved.

* Hydroselenic acid forms no sulphosalts with the metallic sulphobases, but the metallic selenibases produce SELENISALTS by mixing with the combinations of selenium the metals the oxydes of which play the part of acids.

* The minutest quantities of the metallic seleniurets may be easily recognised by the odour which these compounds exhale before the blow-pipe.

7. HYDROTELLURIC ACID, Te+H.

[ACIDE TELLURHYDRIQUE.]

(*Telluretted Hydrogen.*)

* HYDROTELLURIC ACID in the pure state is gaseous, and its odour resembles that of sulphuretted hydrogen. It reddens litmus paper, and is soluble in water. The solution is colourless; but by exposure to the air, tellurium is deposited in the form of a brown powder.

* Hydrotelluric acid forms with metallic oxydes METALLIC TELLURIDES, which appear to have properties analogous to those of the metallic sulphurets; which analogy extends to those found in the natural state. When, however, the metallic tellurides are digested with nitric acid, the tellurium does not appear to require more time to become oxydised or dissolved than the metal with which it is combined. The solution often very easily yields crystals, which are a combination of the metallic oxyde with tellurous acid.

* When the metallic tellurides are roasted in a glass tube by the flame of the BLOW-PIPE, a sublimate of tellurious acid is obtained. If, then, an odour of horse-radish be observed, it is a proof that the telluride contained some selenium.

8. HYDROCYANIC ACID, CyH.

(Acide Cyanhydrique).

* HYDROCYANIC ACID is a hydracid with compound radical. It is produced by the combination of cyanogen (carburet of nitrogen) and of hydrogen. Although, properly speaking, it belongs to the series of organic substances, without which it cannot be produced, yet its very high importance demands that we should relate here the properties by means of which it can be detected, and distinguished from other substances.

* In the pure state, hydrocyanic acid is a colourless, highly volatile liquid, which has a very strong, peculiar odour. Its odour is generally compared to that of the distilled water of bitter almonds, in which it exists; but it is far from being as agreeable. On the contrary, the odour is unpleasant, and when the acid is pure it is irritating and exceedingly poisonous. Pure hydrocyanic acid may be solidified by exposure to an intense cold; and as it is very volatile, even at a low temperature, its evaporation produces a degree of cold sufficient to cause solidification. It is spontaneously decomposed, even out of the contact of the air; the decomposition takes place sometimes rapidly, sometimes slowly. The acid first assumes a reddish-brown colour, then a deep brown, and a carbonaceous matter is deposited; ammonia is formed at the same time, which combines with the undecomposed portion of the acid. The anhydrous acid is seldom prepared, on account of its highly poisonous property.

* Hydrocyanic acid dissolves easily, and in all proportions, in water; the solution exhales the odour of the acid, except that it is weaker in proportion to the quantity of water with which the acid is combined. It is likewise very soluble in alcohol. Both the aqueous and the alcoholic solutions may be kept for a long time without being decomposed; when, however, the liquor is very concentrated, it generally assumes a slightly brownish tinge after the lapse of a few months.

* CONCENTRATED MURIATIC ACID decomposes the concentrated aqueous hydrocyanic acid, which in a short time assumes the form of a crystalline mass, which, according to Pelouze, is composed of muriate of ammonia and of formic acid.

* SULPHURIC ACID decomposes hydrocyanic acid in the same way, but more slowly, and with more difficulty. Hydrocyanic acid is thereby converted into sulphate of ammonia and formic acid: but when an excess of undiluted sulphuric acid has been employed, the formic acid is transformed into carbonic oxyde and water.

* Hydrocyanic acid forms with the metallic oxydes, compounds called METALLIC CYANURETS OR CYANIDES. When an excess of an alkaline solution is poured into aqueous hydrocyanic acid, the odour of the latter disappears, and a cyanide of alkalisable metal is formed. The same phenomenon does not take place with the distilled water of bitter almonds and of cherry laurel (*prunus lauro-cerasus*), although they contain hydrocyanic acid, because this odour is not altogether dependent upon the acid, but likewise upon the presence of an essential oil (*hydroguret of benzoile.*)

* Hydrocyanic acid has a strong affinity for some metallic oxydes, or more properly the cyanogen of the acid has a strong affinity for certain metals, whilst its affinity for other metals is, on the contrary, very weak. The solutions of several of these cyanides are very easily decomposed. To this category the combinations of cyanogen with the alkalies and with the alkaline earths belong. Although these combinations undergo no decomposition by exposure to a red heat out of the contact of the air, yet their aqueous solutions, which have always a reaction similar to that of the alkalies, are easily decomposed when left exposed to the air, or when heated in open vessels. The result of this decomposition is, that the cyanogen and the water become reciprocally converted into ammonia, and into a formiate of alkali. If the cyanides of the alkalisable metal contain an excess of alkali, calcining transforms them also into ammonia and a formiate of alkali; and if the calcining is continued, the water of the

alkali decomposes the latter salt into carbonate of alkali and hydrogen gas.

* Several of the combinations of cyanogen with the metals properly so called, are not decomposed by the strong acids. Such is the case, for example, with *cyanide of silver, cyanide of mercury*, &c., which resist the action of *sulphuric* and of *nitric acid*[1]. Most metallic cyanides appear to be decomposed by MURIATIC ACID, by which they are converted into metallic chlorides, and which liberates the hydrocyanic acid, only it is necessary not to employ an excess of muriatic acid, because in such a case the hydrocyanic acid would be decomposed in the manner above mentioned.

* Free hydrocyanic acid may be recognised in its aqueous solution, both by its peculiar odour, and by means of the following re-agents.

* A solution of NITRATE OF SILVER produces in a solution of pure hydrocyanic acid, an immediate white precipitate, which, by stirring the liquor, is easily separated: it is insoluble in dilute nitric acid, but soluble in free ammonia. The odour of the hydrocyanic acid disappears by the addition of the solution of silver. The precipitate of cyanide of silver thus formed is almost insoluble in water. When *nitrate of silver* is precipitated by a large excess of hydrocyanic acid, so that the odour of the acid is strongly perceptible in the liquid, the liquor filtered from the precipitated cyanide of silver assumes only an opaline tinge by the addition of *muriatic acid*, and does not produce any abundant precipitate of chloride of silver. On the contrary, cyanide of silver is not insoluble in an excess of solution of *nitrate of silver*, which, however, if sufficiently dilute, does not appear to dissolve the smallest portion of cyanide of silver. Cyanide of

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[1] Cyanide of silver and cyanide of mercury are easily decomposed by muriatic acid and by sulphuretted hydrogen. The latter is soluble, without decomposition, in nitric acid; and according to Berzelius, if concentrated sulphuric acid be poured upon cyanide of mercury, it swells into a mass like starch paste, evolving at the same time a slight odour of hydrocyanic acid, and if heat be applied, sulphate of mercury is produced, the cyanogen being decomposed at the expense of the acid; ammonia is liberated, and carbonic and sulphurous acid are evolved.—ED.

silver is completely soluble in a solution of cyanide of potassium, but dilute *nitric acid* precipitates it from such a solution by decomposing the cyanide of potassium. If a solution of *nitrate of silver* be added to the distilled water of bitter almonds, or of laurel, an opaline tinge only is generally produced, and a small portion of the hydrocyanic acid contained in the liquor is precipitated in the state of cyanide of silver. This effect is produced only when a solution of *nitrate of silver,* to which an excess of *ammonia* has been added, is employed, so that the precipitate produced is re-dissolved by the ammonia. The mixture being stirred is now to be rendered slightly acid by pouring a little nitric acid therein, which determines the entire separation of all the cyanide of silver.

* Poured in a solution of NITRATE OF SUBOXYDE OF MERCURY, hydrocyanic acid immediately reduces suboxyde of mercury, and metallic mercury is deposited, whilst a protocyanide of mercury (*cyanure mercurique*) remains in solution. The distilled water of bitter almonds determines also this reduction of suboxyde of mercury.

* When hydrocyanic acid is poured in a solution of ACETATE OF COPPER, a yellowish-green precipitate, of protocyanide of copper, is produced, which gradually becomes more green, and consists then of a mixture of subcyanide and of protocyanide of copper; cyanogen is disengaged. This precipitate is decomposed and dissolved by muriatic acid. It is converted by dilute sulphuric acid, and also by dilute nitric acid, into white subcyanide of copper. Analogous phenomena are produced when hydrocyanic acid is poured in a solution of PROTOSULPHATE OF COPPER.

* A solution of PROTOXYDE or of PEROXYDE OF IRON is not altered by hydrocyanic acid, but if a little alkali be added to the latter acid, it invariably produces a precipitate in the solutions of iron[1]. If the solution operated upon be one of peroxyde of iron, perfectly free from protoxyde, a precipitate of a pure

reddish-brown colour is produced, which is nothing else than peroxyde of iron, and which is perfectly soluble in dilute muriatic acid. If the solution operated upon be one of protoxyde of iron, but containing peroxyde of iron at the same time, the precipitate produced has ordinarily a bluish-green colour. When dilute muriatic acid is poured upon this green precipitate, the excess of protoxyde of iron, and the peroxyde of the same metal, are dissolved, and there remains a blue precipitate (Prussian blue), which often requires a long time to settle, and which sometimes has a greenish tinge[1].

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[1] The alkali necessary to form the alkaline cyanide requisite for the production of the blue precipitate may be added either before or after the application of the solution of the salt of iron.—ED.

* In order to detect the presence of hydrocyanic acid by the production of Prussian blue, the best way is to employ a solution of common *protosulphate of iron, which has been left for a short space of time exposed to the contact of the air,* in order to determine the formation of a sufficient quantity of peroxyde of iron. This is the method most usually resorted to for the purpose of detecting hydrocyanic acid without fear of error. The solutions of the cyanides of alkalies are likewise converted into Prussian blue by *a solution of iron containing at the same time both protoxyde and peroxyde of iron;* as, however, these solutions of cyanides generally contain an excess of alkali, it is advisable also in this case, after having used the solution of iron, to add a little dilute muriatic acid[2]. The solutions of other metallic cyanides, for

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[1] If concentrated or moderately strong muriatic acid be employed, the precipitate is always of an exceedingly rich blue colour, insoluble in water and in muriatic acid, and after being thoroughly washed, soluble in oxalic acid and in binoxalate of potash; the odour of hydrocyanic acid is generally perceptible in this solution.—Ed.

[2] The method here described is known under the name of Scheele's test for free hydrocyanic acid: it may be thus recapitulated.

To the solution suspected to contain free hydrocyanic acid, add—

1st. A little hydrate of potash, and stir the mixture.

2nd. Some solution of common sulphate of iron, which has been for a short time exposed to the air, and stir the whole again.

3rd. An excess of muriatic acid.

The blue precipitate, insoluble in water and in muriatic acid, which will then be formed, may be considered as a certain proof of the presence of hydrocyanic acid in the original solution.

According to Mr. Witting, (Archiv. der Pharm. vi. 112), the presence of hydrocyanic acid in cases of medico-legal chemistry, may be detected in a certain manner, as follows:—The mass suspected to contain the poison is mixed with one-sixth of example, that of *cyanide of mercury* (*cyanure mercurique*), are not precipitated by the solutions of iron[1]. The hydrocyanic acid contained in the waters distilled from various vegetables, for example, from bitter almonds, laurel, &c., may likewise produce Prussian blue by the process just indicated; but the characteristic odour of these waters never disappears with the formation of the precipitate, for the reason given above (page 481).

* The solutions of the persalts of mercury, of lead, and the salts of baryta, produce no precipitates in those of hydrocyanic acid.

* The cyanides of the metals which produce alkalies and alkaline earths are not decomposed, as has been said before, by exposure to a red heat, provided they be not mixed with an excess of base. The combinations of cyanogen with the metals, properly so called, are decomposed in various ways by exposure to a high temperature. Some, being heated out of the contact of the air, are converted into metallic carburets under disengagement of nitrogen; and if the heat has not been too strong, these carburets are pyrophoric, as is the case, for example, with the cyanides of lead and of zinc. Other metallic cyanides, when heated, disengage cyanogen, and leave a residuum of the pure metal, which is the case with the *dry cyanide of silver*[2],

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alcohol, and one-fourth of the mixture is distilled. If hydrocyanic acid be present, it may be instantly detected by the odour of the distilled product. A little caustic potash, however, is added thereto, and a solution consisting of proto and perchloride of iron, which produces a blue precipitate of Prussian blue. If the poisoning has taken place by cyanide of potassium, of zinc, or other cyanides, a little muriatic acid must be added to the alcohol previous to dissolving.—Ed.

[1] In order to detect cyanogen in *cyanide of mercury*, by Scheele's test as above, Dr. Fresenius proceeds as follows:—The solution under examination is to be mixed with muriatic acid and iron filings. Mercury is thereby precipitated, and hydrocyanic acid and protochloride of iron are formed, the latter partially passing into the state of perchloride by contact with the air. An addition of potash, as stated in the preceding note, will now produce ferrocyanide of potassium and ferrosoferric oxyde in the solution, from which the further addition, or an excess of muriatic acid, will precipitate Prussian blue. Cyanide of mercury, however, is readily decomposed by sulphuretted hydrogen, which converts it into sulphuret of mercury and hydrocyanic acid; it is also readily decomposed by hydriodic and muriatic acids, by which it is transformed into an iodide or a chloride, and into hydrocyanic acid.—Ed.

[2] If the cyanide of silver contains water, both hydrocyanic acid and cyanogen are disengaged, and the residuum is a mixture of silver and charcoal.—Ed.

cyanide of mercury, &c. Most of them, on the contrary, yield cyanogen and nitrogen gases, and leave a residuum of a mixture of the reguline metal and of metallic carburet.

* CYANOGEN, which is disengaged in these operations, is a colourless gas, of a pungent and peculiar odour, differing from that of hydrocyanic acid. It may be condensed by pressure into a colourless liquid. When set fire to, it burns with a bluish flame tinged with red. It is slightly soluble in water, and the solution has the same odour as the gas. Mercury does not absorb cyanogen gas, but it is absorbed by the solutions of the alkalies, with which it forms liquids of a brown colour.

* The metallic cyanides, like the metallic sulphurets and fluorides, produce double compounds by uniting with each other. The compounds are not formed in a direct manner by the combination of the cyanides of the metals, the oxydes of which play the part of powerful acids with basic metallic cyanides. The cyanides which principally combine with other metallic cyanides, are those of iron; yet the combinations of cyanogen with *zinc, cadmium, manganese, cobalt, nickel, copper* (especially the *protocyanuret of copper*), *mercury, silver, gold, platinum, palladium,* and *iridium,* produce double cyanides, also by uniting with other metallic cyanurets, principally with the cyanides of the alkalisable metals. Most of these double cyanides may be obtained in very distinct crystals. The ferrous cyanide is a white mass which rapidly absorbs the oxygen of the atmosphere, and soon becomes blue by exposure, on account of a formation of Prussian blue. The ferric cyanide is unknown in the state of purity: but the double cyanides, which both these cyanides form with other metallic cyanides, are the most important, and the best known of all these combinations.

* Among the metallic FERROCYANIDES, those which are formed by uniting with the cyanides of the metals of the alkalies or of the alkaline earths are soluble in water; most of those which are formed by the cyanides of the earthy metals, or of the metals

properly so called, are insoluble in this menstruum, and ordinarily they are likewise insoluble in the free acids. The solutions of FERROCYANIDE OF POTASSIUM, by means of which the production of the double cyanides is determined by pouring it in the solutions of the earths, and of the metallic oxydes properly so called, is therefore an available re-agent for the detection of these oxydes. Wherefore, in the preceding pages, in speaking of the behaviour of the re-agents towards the bases, I have fully described the reactions produced by a solution of ferrocyanide of potassium in those of the various metallic oxydes. The metallic ferrocyanides which have the metals of the alkalies or of the alkaline earths for a base, have all a light-yellow colour when crystallised. They are only slowly decomposed by exposure to a red heat out of the contact of the air. The ferrous cyanide is converted into carburet of iron, whilst nitrogen gas is disengaged, but the cyanide of the alkaline metal is not decomposed. The metallic ferrocyanides which have the cyanides of the metals properly so called for a base, undergo, by exposure to a red heat in closed vessels, a decomposition, in consequence of which sometimes the metallic cyanide is reduced to the state of metal which remains with the carburet of iron formed at the expense of the cyanide of iron, cyanogen being at the same time disengaged: sometimes also there remains a double metallic carburet, and nitrogen only is disengaged.

* The presence of protocyanide of iron (*cyanure ferreux*) in solutions of the metallic ferrocyanides which have the metals of the alkalies or of the alkaline earths for a base, cannot be detected by the re-agents which are ordinarily employed for testing iron. One would expect that in these solutions the iron should behave in the same manner as in a solution of protosalt of iron, but all the re-agents which have been mentioned (pages 83 to 88) produce no change in the solutions of the metallic ferrocyanides, without excepting even hydrosulphuret of ammonia. The free acids alone, principally if concentrated, produce in these solutions, especially with the help of heat, precipitates which at first are white, and consist of protocyanide

of iron, but which by the contact of the air soon become blue, and converted into Prussian blue. In this reaction the metallic cyanide combined with the ferrous cyanide is decomposed, and hydrocyanic acid is disengaged. Even the dilute acids determine this reaction, but then it is less distinct, and a longer time is required than when the acids are concentrated. Ordinarily, in such cases, when the solution is very dilute, not the least white precipitate is produced; but in course of time an inconsiderable blue precipitate appears. On this account the solution of *ferrocyanide of potassium* is not a very available re-agent for the solutions of the metallic oxydes when these solutions are acid, for the tint of the coloured precipitates is always more or less modified by the admixture of blue, from the cause just mentioned. *Nitric acid* does not in course of time produce any blue colour in these solutions, but it slowly communicates to them a brown colour, because the cyanogen is decomposed.

* When the presence of iron is desired to be ascertained in a precise manner in the metallic ferrocyanides, it is necessary either to expose them for a long time to a *red heat in contact with the air*, by which means the iron is converted into peroxyde of iron, which may then be detected by the usual reagents after having dissolved it in an acid; or else they are to be treated with *hot fuming nitric acid*, to which muriatic acid is subsequently added, by which process a solution of peroxyde of iron is likewise obtained; or lastly, they may be heated with *sulphuric acid* until the excess of this acid has nearly all evaporated. The solution of a metallic ferrocyanide may also be recognised by the precipitates which it gives with the solutions of the different metallic oxydes, especially with that of peroxyde of iron (page 90).

* Among the METALLIC FERRICYANIDES, for the discovery of which we are indebted to L. Gmelin, those only are soluble in water which contain a cyanide of a metal of alkali or of alkaline earth. They are of a red colour. Nearly all those which contain metals, properly so called, are insoluble, and each has a

characteristic colour. This fact has induced me in the preceding pages, when explaining the behaviour of the bases towards re-agents, fully to detail the reactions produced by the *ferricyanide of potassium* in the solutions of the various metallic oxydes. One might be inclined to think that the iron contained in the solutions of the metallic ferricyanides would behave like peroxyde of iron, but the usual re-agents fail in this respect as completely as with the solutions of the metallic ferrocyanides. In order to detect the presence of iron in these combinations, they must be strongly heated in contact with the air, or else treated by fuming nitric acid and muriatic acid, or by sulphuric acid. When treated by the acids, the solutions of the metallic ferricyanides become green, and a small quantity of blue precipitate is deposited in course of time. Wherefore, ferricyanide of potassium is in some cases a test of but little value, especially when the solutions of metallic oxydes under examination are acid. When these combinations are heated out of the contact of the air, the first impression of the heat seems to convert them into the corresponding ferrocyanides under disengagement of cyanogen and nitrogen, and a small quantity of carburet of iron is left as residuum; a stronger heat further decomposes these cyanides in the manner mentioned before.

* As to the double cyanides which result from the combination of other metallic cyanides with the cyanides of the alkaline metals, the presence of the metal cannot be detected in many of them, when soluble, by means of the usual re-agents, even sulphuretted hydrogen and hydrosulphuret of ammonia. According to Rammelsberg, the metal of the double cyanides of silver, mercury, and of cadmium especially, may be easily and completely precipitated in the state of metallic sulphurets by the two above-named re-agents; but the double cyanides of copper, zinc, cobalt, nickel, manganese, cannot be thus precipitated at all, or, at any rate, a certain lapse of time is required, and even then the precipitation is not complete.

* The combination of cyanogen and of sulphur with hydrogen produces HYDROSULPHOCYANIC ACID. It is a colourless, strongly

acid liquid; its odour is pungent, but does not at all resemble that of hydrocyanic acid. This acid boils at about the temperature of boiling water.

* Hydrosulphocyanic acid forms with the metallic oxydes compounds called METALLIC SULPHOCYANIDES, amongst which those which contain an alkalisable metal are soluble in water; these solutions are colourless, and are distinguished principally because, when a solution of peroxyde of iron is poured in them, no precipitate is produced, but the liquid assumes a blood-red tinge so deep in colour, even when the smallest possible quantity of peroxyde of iron has been used, that the solution of SULPHOCYANIDE OF POTASSIUM may rightly be looked upon as the most delicate re-agent for the detection of the minutest traces of peroxyde of iron. The solution of *sulphocyanide of potassium* produces also a very distinct blood-red colour in one of peroxyde of iron, even when hydrosulphuret of ammonia fails in tinging it black. The red colour of the liquor bears some analogy with that produced by mixing the solutions of peroxyde of iron with those of acetates or of formiates, but it is much more intense. The solution of *sulphocyanide of potassium* produces no red colour in those of protosalts of iron when they are perfectly free from peroxyde of iron, but the red colour soon makes its appearance if the liquor be left exposed to the air; wherefore the red colour of the liquid disappears when *iron filings* are dropped into it and left therein for some time. The addition of a small quantity of a free acid does not alter the blood-red colour of the liquid; the addition of a larger quantity renders it somewhat lighter. A sufficient quantity of *nitric acid* destroys it completely, but only after some time; and the addition of a solution of *peroxyde of iron* does not restore it. *Oxalic, iodic, phosphoric* and *arsenic* acids destroy also this colour, but then it is restored by the further addition of the solution of a persalt of iron. The solution of *protochloride of tin*, or of sulphuretted hydrogen, destroys it very rapidly, and so does *sulphurous acid*, but not in the cold. The red colour is instantly destroyed by ammonia, and a precipitate

of peroxyde of iron is produced at the same time. Hydrosulphuret of ammonia produces therein a black precipitate of sulphuret of iron.

* The solution of *sulphocyanide of potassium* mixed with a solution of PROTOXYDE OF COPPER, provided the two liquors be not too dilute, yields a black precipitate insoluble in muriatic acid. When the two liquors are dilute, a green tinge only is thus imparted to the mixture, and if to this green liquor a little solution of *protochloride of tin* in dilute muriatic acid be added, a white precipitate of sulphocyanide of copper is instantly formed. This precipitate being produced in even very dilute liquids, *sulphocyanide of potassium* is therefore a useful re-agent for the detection of proto and of suboxyde of copper, the latter oxyde being of course precipitated also without addition of protochloride of tin. The black precipitate is likewise instantly converted into a white one by solution of protochloride of tin, and the same effect is produced by long standing.

* The solution of sulphocyanide of potassium produces in solution of NITRATE OF SILVER a white precipitate insoluble both in dilute nitric acid and in ammonia.

* A solution of NITRATE OF SUBOXYDE OF MERCURY is reduced by one of sulphocyanide of potassium, as by hydrocyanic acid.

SECTION III.

SIMPLE BODIES.

1. OXYGEN, O.

(Oxygène.)

* **Oxygen** is a colourless and inodorous gas, almost insoluble in water, and which produces no change in lime-water, nor in tincture of litmus. It is heavier than atmospheric air, its specific gravity being 1·1026. That which principally distinguishes it from other gases is its property of supporting the combustion of combustible bodies in a most vivid manner; wherefore, when a glimmering splinter is plunged in a jar full of this gas it is immediately kindled, and burns therein much more vividly than in atmospheric air. Several gases, which cannot of themselves support combustion, acquire this property by being mixed with oxygen gas; wherefore, combustible bodies can burn in atmospheric air.

* When oxygen gas, or substances which contain oxygen gas, such as atmospheric air, are mixed with hydrogen gas, or with gases in the composition of which hydrogen gas enters, such as sulphuretted hydrogen, &c., and the mixture is set fire to, a violent detonation ensues, accompanied by a diminution of the volume of the mixed gases. As, in this experiment, one volume of oxygen gas combines exactly with two volumes of hydrogen gas to produce water, it is easy to determine, from the quantity of gas which has disappeared, that of the oxygen which was contained in the mixture.

2. HYDROGEN, H.

(*Hydrogène.*)

Hydrogen is a colourless and inodorous gas, which, however, acquires a disagreeable smell from being mixed with small portions of foreign substances. It may be inflamed, and burns then with a flame which is hardly visible by daylight. Mixed with oxygen gas in a glass jar, it burns with a violent explosion upon the mixture being inflamed. The diminution of volume which results from this experiment may serve to determine the quantity of hydrogen which was contained in the mixture, since it forms the two-thirds of the gas which has disappeared. Hydrogen gas is the lightest of all known substances; its specific gravity, compared to that of atmospheric air, being only 0·0688.

3. NITROGEN, N.

(*Nitrogène* or *Azote.*)

* **Nitrogen** is a colourless and inodorous gas, which is more difficult to recognise than any other gas. It cannot support combustion, in consequence of which the ignited bodies which are plunged into it are immediately extinguished. It cannot be inflamed, a property by which it is distinguished from hydrogen gas. It does not render lime-water turbid. Its specific gravity, compared with that of atmospheric air, is 0·976. When mixed with several other gases, there is often no other way of ascertaining its presence than by separating quantitatively the other gases which are mixed with it. The method which has been proposed for its detection, and which consists in mixing it with oxygen and hydrogen gases, inflaming the mixture by the electric spark, and testing the residuum for nitric acid by means of concentrated sulphuric acid and solution of sulphate of iron, is not applicable, at least with respect to the gaseous mixtures which may be detonated. (See the second part of this Manual).

4. SULPHUR, S.

(*Soufre.*)

* SULPHUR is solid at the ordinary temperature. It has a conchoidal fracture, and a yellow colour. It is translucent, rarely transparent, when obtained in the crystallised state by means of certain solvents, or as found in nature. After fusion and subsequent cooling it is transparent, but it soon becomes completely opaque. The sulphur which is precipitated in the form of powder from the solutions which contain sulphuretted hydrogen is whitish; such is the case, for example, with the sulphur which is precipitated, by exposure to the air, from a solution of sulphuretted hydrogen, or from the solutions of the alkaline sulphurets to which an acid is added. But pulverulent sulphur regains its usual yellow colour when precipitated from solutions which do not contain sulphuretted hydrogen, for example, from the solutions of the hyposulphites to which an acid is added. Sulphur is brittle, and when set fire to, burns in the air with a blue flame, and emits the odour of sulphurous acid. The result of the combustion of sulphur, even in oxygen gas, is always sulphurous acid, and never sulphuric acid. The specific gravity of sulphur, compared to that of water, is 1·98.

Sulphur begins to melt at a temperature somewhat higher than boiling water, and in that state it is perfectly liquid. If the temperature be increased, it thickens, turns brown and viscid; but by lowering the temperature it again resumes its fluidity. If water be poured upon sulphur brought by fusion to the viscid state, a brown viscid mass is obtained, which requires a long time to become again solid, brittle, and yellow. If the sulphur which is brought by fusion to the viscid state be heated still more strongly, and as much as possible out of the contact of the air, it boils, and becomes converted into an orange-yellow gas, similar in point of colour to the vapours of fuming nitric acid. This gas, being set fire to, burns in the air with a blue flame like sulphur, and emits likewise an odour of sulphurous acid. Sulphur may easily be recognised by this odour, even when its exterior appearance is altogether concealed by other substances with which it may be mixed.

* If sulphur be digested or boiled for a long time with ordinary nitric acid, it dissolves therein, because it is thereby converted into sulphuric acid. Its complete solution in nitric acid, however, is very difficult, and requires that the nitric acid be frequently renewed. The complete solution of sulphur is more rapid in fuming nitric acid. *Muriatic acid* has no action upon sulphur. *Aqua regia*, on the contrary, has more action upon it than nitric acid alone. When a current of *chlorine* gas is passed through pulverised sulphur, it is converted into chloride of sulphur. A solution of pure *potash* dissolves sulphur, especially by boiling: the solution contains then sulphuret of potassium and hyposulphate of potash. A solution of carbonate of potash likewise dissolves sulphur, and produces the same reaction; but the whole with more difficulty than pure potash. *Ammonia* has no action upon sulphur. When sulphur is fused with a nitrate of fixed alkali, a sulphate of alkali is formed.

5. SELENIUM, Se.

(Sélénium.)

* SELENIUM is solid and brittle at the ordinary temperature; its fracture is conchoidal, and has a metallic lustre; its colour is black or dark grey; it is opaque. Drawn into fine threads, it is translucid, and of a ruby colour. Reduced into very fine powder it is of a very deep red colour. Separated by means of sulphurous acid, zinc, or otherwise, from a solution of selenious acid, it forms a bulky powder, of a cinnabar-red colour. By boiling, the powder becomes agglomerated and black. The specific gravity of selenium is 4·32.

* When selenium is heated, at first it softens, then becomes viscid, and lastly it fuses. If heated more strongly still, and as much as possible out of the contact of the air, it boils and evaporates. The gas thus produced has a yellow colour, but less deep than that of gaseous sulphur. In contact with the

air it burns with a blue flame when kindled. However small the quantity may be, it exhales, when heated, an odour of decayed horse-radish, which is highly characteristic, and by which it may be very easily recognised. Heated in contact with the air, but without making it red hot, red fumes only are evolved, which consist of selenium in powder; but the odour of decayed horse-radish requires a stronger heat to become perceptible.

* Selenium is somewhat difficultly oxydised, and dissolved by *nitric acid,* and by *aqua regia,* but much more easily than sulphur; in both cases selenious acid is formed without the slightest trace of selenic acid; [this action is analogous to that on sulphur]. Selenium is not soluble in *muriatic acid.* When a current of chlorine gas is passed over heated selenium, the result is the formation of either liquid chloride of selenium, or if the chlorine be in more abundant quantity, solid chloride of selenium. Selenium is dissolved, but more difficultly than sulphur, in a solution of pure potash, with the help of heat. If sulphuret of selenium be boiled with a solution of potash, the sulphur is first dissolved, and if there is not a sufficient quantity of potash present, the pure selenium remains. When selenium is fused with a *nitrate of fixed alkali,* a seleniate of alkali is produced.

6. PHOSPHORUS.

(*Phosphore.*)

* At the ordinary temperature phosphorus is solid, of a white translucid colour, soft as wax, and heavier than water. Its specific gravity is 1·77. It fuses as soon as the temperature reaches + 35° cent. (95° Fahr.), and consequently in hot water. In close vessels it may be volatilised and distilled by exposure to a greater heat. The gas thus produced is colourless.

* In contact with the air, phosphorus is very easily inflamed, a slight friction being often sufficient to determine this effect. In summer, when the temperature is great, it often inflames spontaneously, especially when resting upon uneven substances (as, for example, upon coarse brown paper), and even in winter

very trifling and often unforeseen causes are sufficient to determine its inflammation. It burns with an intense flame, and with a thick white smoke. It is luminous in the dark, a property which is more distinct when plunged in nitric acid, so as to be a little above the level of the liquid. Exposed to the air it emits white fumes[1].

* It is dissolved more easily than sulphur by *nitric acid* and *aqua regia*, and is converted by them into phosphoric acid. When a large quantity of phosphorus is digested or boiled for a long time in less nitric acid than is necessary completely to oxydise it, a mixture of phosphorous and of phosphoric acid is produced. Phosphorus is insoluble in muriatic acid. When after being previously heated it is exposed in a current of gaseous chlorine, it inflames, and is thereby converted into solid perchloride of phosphorus, or into liquid chloride of phosphorus, according to the quantity of chlorine employed. Phosphorus is soluble in a solution of pure potash, with disengagement of phosphuretted hydrogen (*phosphure trihydrique*). The solution then contains phosphate and hypophosphite of potash. When however, after the phosphorus has completely dissolved, the whole is again boiled for a long time in an excess of potash, the liquor is found to contain phosphate of potash only; for under the influence of the excess of potash, the acid of the hypophosphite is transformed into phosphoric acid under disengagement of hydrogen gas.

* The combinations of phosphorus with the metals called *metallic* phosphurets are as yet imperfectly known. That with potassium, when treated with water, yields phosphuretted hydrogen (*phosphure trihydrique*) and hypophosphite of potash. Phosphuret of calcium and of barium behave in the same manner when they are mixed with phosphate of lime or of baryta. They are obtained in this state by heating these earths and treating them by phosphorus. If these combinations be boiled in water, phosphuretted hydrogen is disengaged, the

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[1] These fumes have a peculiar alliaceous odour, which resembles that of arsenic. —Ed.

hypophosphite of lime or of baryta dissolves in the liquor, whilst the phosphate of lime or of baryta remains insoluble. The combinations of phosphorus with the metals, properly so called, behave in quite a different manner, but only a small number of these compounds has as yet been examined. The combination of phosphorus with iron is insoluble in *muriatic acid,* and dissolves only in *nitric acid* or *aqua regia,* during which operation the phosphorus becomes entirely converted into phosphoric acid. Phosphurets of copper, of nickel, and of cobalt behave in the same manner.

7. CHLORINE.

(*Chlore.*)

* Pure chlorine is a gas of a yellowish-green colour, which may be condensed by pressure into an oleaginous liquid of a deep green colour. Chlorine gas has a suffocating smell. It is heavier than atmospheric air, its specific gravity being 2·47. It may support the combustion of several substances. By uniting with a small quantity of water, chlorine forms a crystalline combination of a light yellow colour; it is soluble in a larger quantity of water, yet not in very considerable proportion. The solution has the odour of gaseous chlorine, and like the latter it not only decolorises litmus paper, but likewise it destroys all vegetable colours. It soon undergoes decomposition, a little muriatic acid and a small quantity of chlorous acid being formed in the liquor.

* *Mercury* and most other metals absorb chlorine, and are thereby converted into *metallic chlorides.* It is absorbed also by the solutions of the fixed alkalies which are thereby converted into metallic chlorides, and into chlorates of alkalies. The same phenomena are produced by the carbonates of alkalies, but the reaction is accompanied by a disengagement of carbonic acid; and by the strong bases, but in such a case chlorites are formed instead of chlorates, which chlorites remain mixed with the metallic chlorides. Oxyde and a few salts of silver are likewise converted by chlorine gas, with the inter-

mediary of water, into chloride and into chlorate of silver, wherefore chlorine gas, perfectly freed from muriatic acid, when passed through a solution of nitrate of silver, always produces a precipitate of chloride of silver. Chlorine gas is absorbed by *ammonia* with disengagement of nitrogen gas. When chlorine gas is passed through the solutions of the neutral ammoniacal salts, chloride of nitrogen is formed, an oleaginous liquid which detonates in the most violent manner when slightly heated, or by contact with combustible substances.

8. BROMINE, Br.

(*Brôme.*)

* At the ordinary temperature bromine is a liquid of a deep reddish-brown colour, of a peculiar and disagreeable odour analogous to that of chlorine gas. It is much heavier than water, its specific gravity being 2·966. It boils at about +50° cent., and is thereby converted into a reddish-brown gas. At a temperature of —23° or 24° cent. it forms a crystalline mass of a leaden-grey colour, which has almost a metallic lustre. It combines with a small quantity of water by which it is transformed into a crystalline hydrate. A larger quantity of water dissolves it but sparingly; the solution has a hyacinth-red colour. Like chlorine, bromine bleaches litmus paper, and destroys the other vegetable colours; it behaves also like chlorine towards the metals, and the solutions of the pure alkalies, of the carbonates of alkalies, and of other powerful bases.

9. IODINE, I.

(*Iode.*)

* At the ordinary temperature, iodine is a solid crystalline body, of a black [steel-grey] colour. It is heavier than water, and its odour is analogous to that of chlorine, but is much weaker. It begins to fuse at a temperature somewhat above that of boiling water; and heated more strongly still, it evaporates. Gaseous iodine has a fine violet-red colour, which is quite

characteristic. Iodine is sparingly soluble in water, but it dissolves more easily therein when the water contains certain salts, especially metallic iodides. It does not destroy vegetable colours so readily nor so effectually by far as chlorine and bromine. It combines with various vegetable substances (for example, with starch), with which it forms a blue compound, by means of which the minutest quantities of iodine may be detected, especially when the iodine is dissolved in alcohol, in which it is very soluble. Iodine colours the human skin yellow, but after some time the colour spontaneously vanishes[1].

* Iodine behaves like chlorine and bromine towards the metals, and towards the solutions of the pure alkalies and carbonates of alkalies. With *ammonia* it forms iodide of ammonia and iodide of nitrogen; the latter substance separates under the form of an insoluble black powder, which detonates violently by the slightest pressure.

10. FLUORINE, F.

(*Fluor.*)

* FLUORINE has never yet been obtained in a state of purity.

11. CARBON, C.

(*Carbone.*)

* THE various species of carbon differ much from each other in their aspect and properties. The purest carbon constitutes diamond, which is crystallised and colourless, though found sometimes coloured also. Diamond has an extraordinary brilliancy, and is harder than all other bodies. All the other species of carbon, which often contain only very small portions of foreign matter, are black, and are either pulverulent, or solid and porous, but often also they are vitreous, or even crystallised (graphite). All the varieties of carbon are infusible and fixed. Most of them may be burnt in the air, and are thus converted

into carbonic acid or oxyde of carbon, and often slight traces of ashes only are left as residuum. Diamond, however, and graphite require a very high temperature to burn, and their combustion is arrested, in contact of the air, as soon as one ceases to heat them, but it continues in oxygen gas.

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[1] Bromine and also nitric acid colour the human skin yellow likewise, but the colour is permanent; that is, it disappears only with the renewal of the epidermis, which is corroded.—ED.

* Most varieties of carbon are oxydised by boiling in nitric acid; carbonic acid being formed, and the result being a peculiar substance, known under the name of artificial tannin, which is soluble in the excess of acid, to which it communicates a brown colour. Diamond and graphites are not attacked by *nitric acid*, nor even by *aqua regia*. *Chlorine gas* has no action upon carbon, even with application of heat; neither is it attacked by a solution of pure potash; but when fused with the fixed carbonates of alkalies it is converted into carbonic oxyde, which is disengaged, and the residuum consists either of the pure alkali, or of a mixture of alkali and of charcoal, if the latter be in excess. When, carbon being mixed with nitrate of potash, heat is applied, a detonation ensues.

* Carbon combines with hydrogen in a great number of different proportions. Two of these combinations are gaseous, and are called *quadrihydrocarbon* and *dihydrocarbon* (olefiant gas),—[*carbure tetrahydrique* and *carbure dihydrique*]. Quadrihydrocarbon, or protocarburetted hydrogen, burns when set fire to with a feeble blue flame, which is not very luminous. When mixed with oxygen, or with atmospheric air, and set fire to, it detonates: in this experiment it requires its own bulk of oxygen gas to be converted completely into carbonic acid. It is not decomposed by chlorine gas in the dark, except water be present; under the influence of light, chlorine gas does not react upon protocarburetted hydrogen, provided both gases be dry; for if water be present an excess of chlorine gas converts it into carbonic acid and muriatic acid. Protocarburetted hydrogen can never be obtained very pure. I shall fully indicate in the second part of this work what process must be adopted to free it as much as possible from the other gases, which may be mixed with it. Bicarburetted hydrogen, or olefiant gas (*carbure*

dihydrique), being set fire to, burns with an extremely brilliant flame, and its mixture with oxygen or with atmospheric air produces a violent detonation when inflamed. Three times its own bulk of oxygen are required to convert it completely into carbonic acid and water. It combines with chlorine gas, both in daylight and in the dark, and thus produces an oleaginous body, by which character it is principally distinguished from tetrahydroguret of carbon.

* The other combinations of carbon and hydrogen are either solid or liquid. Most of them belong to that class which are called organic substances.

12. BORON, B.

(*Bore.*)

* Boron is a dark-brown powder with a greenish tinge. When exposed to a white heat out of the contact of the air, it skrinks, but does not volatilise. Heated in the air, it burns vividly, and is converted into boracic acid, which, enveloping the, as yet, unburnt portions, shelters them from the contact of the air. It is promptly converted by nitric acid and aqua regia into boracic acid, with the help of heat. It is converted by chlorine gas into gaseous chloride of boron. Fused with pure potash, it absorbs the oxygen of the water contained in the alkali, and is thereby converted into boracic acid, hydrogen being at the same time disengaged. Fused with the carbonates of the fixed alkalies, it becomes oxydised at the expense of the carbonic acid, and carbon is liberated. Mixed with nitrate of potash and then heated, it detonates violently.

13. SILICIUM, Si.

(*Silicium.*)

* Silicium is a deep-brown powder, which externally resembles boron. Heated in contact with the air, part of it burns vividly, and is converted into silicic acid, which shelters the remainder from the contact of the air. During this experiment the silicium

assumes a lighter colour. The portion which has not burnt has become so altered that it is no longer susceptible of being oxydised by the contact of the air, or in oxygen gas even at a high temperature. In this state silicium can be dissolved only by a mixture of nitric acid and of hydrofluoric acid. When silicium is mixed and heated with a carbonate of fixed alkali, it becomes easily oxydised at a temperature below white heat, a silicate of alkali is formed, carbonic oxyde gas is disengaged, and carbon is liberated. Nitrate of potash acts in the like manner; when silicium is mixed with this salt, it is necessary to expose it to a white heat to oxydise it. If a current of chlorine gas be passed over silicium and heat applied, chloride of silicium is formed.

14. TANTALUM, Ta.

(*Tantale.*)

* Tantalum is a black powder, which, being heated in contact with the air, burns, and is converted into tantalic acid. It is not attacked by nitric acid, nor by aqua regia, nor by a solution of pure potash. It is soluble only in hydrofluoric acid, with disengagement of hydrogen gas. Fused with the alkalies or carbonates of alkalies it is oxydised. Its behaviour at a high temperature in contact with the steam of water has not been examined.

15. TELLURIUM, Te.

(*Tellure.*)

* Tellurium has a metallic lustre. Its colour resembles that of silver; its structure is very lamellar: it is brittle, easily fusible, and conducts electricity like the other metals, but more feebly. When strongly heated out of the contact of the air, it may be volatilised; heated in contact with the air, it rapidly absorbs oxygen and is converted into tellurous acid, which is disengaged in the form of a white smoke. When tellurium is oxydised upon charcoal by means of the blow-pipe, the flame assumes a blue colour. Its specific gravity is 6·115. Tellurium

is very soluble in nitric acid, and in aqua regia its solution contains tellurous acid, which very soon separates in the state of anhydrous acid if the liquor be not diluted with water, in which case aqueous tellurous acid is formed. Tellurium is insoluble in muriatic acid, and in solution of potash. It is not attacked in the cold by chlorine gas, but with the help of a gentle heat, if there be an excess of chlorine, perchloride of tellurium ($Te\ Cl_2$), and if there be an excess of tellurium, chloride of tellurium ($Te\ Cl$), is formed. Metallic tellurium does not decompose water even at a very high heat.

16. ARSENIC, As.

(*Arsenic.*)

* Arsenic, prepared artificially, forms crusts having the metallic lustre, and sometimes crystalline masses of a steel-grey colour.

* The crystals can readily be cleaved, and the fracture, when recent, has a very distinct metallic lustre. The metal retains its brilliancy in a dry atmosphere, but moisture tarnishes it; it then absorbs oxygen, and is converted into suboxyde of arsenic, wherefore metallic arsenic often appears black, and destitute of metallic lustre. Put in contact with water, with free access of the air, it is gradually converted into arsenious acid. It is brittle, and may be easily pulverised; when heated it is entirely volatilised, without first beginning to fuse, and its vapour has a characteristic odour of garlic, by means of which the minutest traces of arsenic can be detected. Heated in contact with the air, it volatilises in the form of a white smoke, which is arsenious acid. At a higher temperature, or when heated in oxygen gas, it burns with a pale blue flame. Its specific gravity is 5·70.

* Arsenic being heated with nitric acid dissolves therein; the solution contains arsenious acid; when arsenic is dissolved in aqua regia, the solution contains arsenic acid. Arsenic is not soluble in muriatic acid; but some arseniurets, such as those of zinc, dissolve in this acid with disengagement of arseniuretted hydrogen (*arseniure trihydrique*). Metallic arsenic does not decompose steam of water even at a high temperature.

17. CHROMIUM, Cr.

(Chrome.)

* **Metallic** chromium has a greyish-white colour. It is brittle, very difficult to fuse, and is not magnetic when pure. It is unalterable in the air, even with the help of heat. It is often obtained in the form of a black powder, which, being heated red-hot in the air, burns, and produces a brown oxyde. Nitric acid or even aqua regia have little or no action upon it; but hydrofluoric acid, especially with the help of heat, dissolves it under disengagement of hydrogen gas: the solution contains chromic oxyde. According to Regnault, it is dissolved also by sulphuric acid, with disengagement of hydrogen gas. At a high temperature this metal decomposes water, and is converted into chromic oxyde, with disengagement of hydrogen gas.

18. MOLYBDENUM, Mo.

(Molybdène.)

* **Molybdenum**, after fusion, is silver-white, and may be slightly flattened under the hammer before breaking to pieces. But owing to its difficulty of fusion it has hitherto been but rarely obtained in the melted state. It is more readily and generally obtained in the state of a grey metallic powder, which may be polished by friction. It is unalterable in the air, but by exposure to a red heat it is converted into molybdic oxyde, and by a protracted calcining it passes into the state of blue oxyde, and finally of molybdic acid. It is not dissolved by muriatic acid, dilute sulphuric acid, and even hydrofluoric acid. Concentrated sulphuric acid converts it into a brown mass with disengagement of sulphurous acid. It is easily dissolved by nitric acid and aqua regia, and converted by them into molybdic acid, provided a sufficient quantity of the re-agent be employed; if the quantity of nitric acid be small, nitrate of molybdenum only is obtained. At a high temperature, molybdenum decomposes steam of water with disengagement of hydrogen gas, and is converted first into blue oxyde and then into molybdic acid, which evaporates as fast as it is produced.

19. TUNGSTEN, W.

(*Tungstène.*)

* Tungsten in masses is steel-grey, pretty brilliant, very hard, brittle, and very heavy[1]. It has but seldom been melted, because it is extremely difficult of fusion. It is more easily procured in the form of an iron-grey powder, which, by friction, acquires a metallic lustre. It is not altered by exposure to the air, but if then brought to a red heat it absorbs oxygen and is transformed into tungstic acid. This phenomenon takes place, especially when it is in the state of powder, under which form the metal burns almost like tinder. Its behaviour towards acids at a high temperature has not yet been examined: it decomposes water, and is converted into tungstic acid, hydrogen gas being disengaged.

20. VANADIUM, V.

(*Vanadium.*)

* In the metallic state vanadium has much resemblance to molybdenum. It is not quite so white as silver, and is very brilliant, but not uniformly so. It is not malleable in the least degree. It is not oxydised either by the contact of air, or of water; but by keeping, it gradually becomes less brilliant, and assumes a reddish colour. It is not dissolved by boiling *sulphuric acid, muriatic,* or *hydrofluoric acids;* but it is soluble in *nitric acid* and in *aqua regia,* the solution is of a fine deep blue colour. It is not dissolved by a boiling solution of hydrate of potash. At a red heat it does not decompose the carbonates of alkalies, as is the case with silicium and zirconium. It is not reduced by metallic zinc in the humid way from its acid, nor from its alkaline solutions. Its behaviour at a high temperature towards aqueous steam is not known.

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[1] Its specific gravity is 17·22, or even 17·6. It is therefore one of the heaviest metals, and inferior only to platinum, gold, and iridium.—Ed.

21. ANTIMONY, Sb.

(*Antimoine.*)

* ANTIMONY has a white colour resembling tin, but with a tinge of blue; it is very brilliant, and has a lamellar texture. It is brittle, easily pulverised, and easily fused. Heated out of the contact of the air, it is slightly volatile only at a white heat. It is not altered by exposure to the air. Heated in contact with the air it remains red hot for a long time after the application of heat has been withdrawn, and emits a thick white smoke of oxyde of antimony, which is deposited at the surface often in the form of brilliant crystals. If a small piece of antimony be heated upon charcoal before the blow-pipe, the metallic bead, after having left off smoking, is found covered with a net-work of crystallised oxyde of antimony. Antimony may be, in contact with the air, completely volatilised under the form of oxyde of antimony. Its specific gravity is 6·71.

* Antimony is easily oxydised by nitric acid, but it is not dissolved by it because all the degrees of oxydisation of this metal are insoluble in that acid. When antimony is treated by nitric acid of ordinary strength, the greatest portion of it is converted almost totally into oxyde of antimony. Antimony is scarcely attacked by hot muriatic acid, although sulphuret of antimony is readily dissolved by that acid. The best solvent of antimony is aqua regia, which dissolves it completely with the help of heat, and the solution contains either oxyde of antimony alone, or, when the digestion has lasted for a long time, a certain quantity of antimonious acid also. When antimony contains much lead, its solution deposits, on cooling, spangles of chloride of lead. If the aqua regia solution of antimony be supersaturated with ammonia, the precipitate obtained should be completely soluble in hydrosulphuret of ammonia; if a black metallic sulphuret be left behind, the operator may conclude that the antimony contained iron, lead, or other foreign metals. If the solution of antimony in aqua regia be diluted with water, it becomes milky, which is not the

case when tartaric acid has been previously added to it. If a current of chlorine gas be passed over antimony, heat being applied to the antimony without raising the temperature too much, a liquid chloride of antimony is obtained. Metallic antimony decomposes water, but at a very high temperature only; it is thereby converted into oxyde of antimony with disengagement of hydrogen gas.

22. TITANIUM, Ti.

(*Titane.*)

* When titanium is in the state of a cohering mass, it has a copper-red colour, which is characteristic, and has a metallic lustre. It is likewise obtained under the form of a black powder, or rather of a dark indigo-blue colour, without metallic brilliancy, but which, however, acquires by friction a metallic lustre of a copper colour. Such as it is found in certain iron scories, titanium is in small cubic crystals, which are hard, brittle, almost infusible and fixed; and when heated in the air they become oxydised only superficially[1]; they are not attacked by muriatic nor by nitric acids, nor by aqua regia, but when fused by a strong heat, with nitrate of potash, they become oxydised, especially by adding a little borax, or carbonate of soda. The titanium obtained in black powder, or in the state of thin spangles of a copper-red colour, is converted into titanic acid by nitric acid, aqua regia, and by the influence of a red heat. At a low red heat, this metal decomposes water, and is converted into titanic acid, with disengagement of hydrogen gas.

23. TIN, Sn.

(*Étain.*)

* Tin has a silver-white colour. It is soft and malleable. It may be reduced into thin plates, and produces a peculiar creaking noise when suddenly bent. When rubbed, and especially with sweaty fingers, it emits a rather disagreeable smell.

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[1] Titanium is extremely hard, and scratches glass, steel, and even agate; and it is insoluble in all acids, except a mixture of nitric and hydrofluoric acids.—Ed.

It is nearly as fusible as lead. In close vessels it cannot be volatilised, or, at least, it requires a very strong heat. It is not altered by the air at the ordinary temperature, but when heated it becomes covered with a pellicle of greyish-white protoxyde of tin. When exposed to a very gentle heat, it often acquires a yellowish tinge. Its specific gravity is 7·285.

Tin is easily oxydised by nitric acid with the help of heat, but the peroxyde of tin which is thus formed remains insoluble. Dilute nitric acid may, however, in the cold, and by carefully and altogether avoiding heat, dissolve tin in a finely-divided state; protoxyde of tin only is then produced. Aqua regia rapidly attacks tin, and powerfully when the metal is finely divided. Yet in order to obtain it in solution, heat must altogether be avoided, and the tin must be introduced into the aqua regia by small portions at a time. This metal is dissolved by muriatic acid under disengagement of hydrogen gas, especially when heat is applied, and provided the acid be not too dilute; the solution does not, however, proceed very rapidly, and the liquor contains protochloride of tin. Concentrated sulphuric acid dissolves tin under disengagement of sulphurous acid. Hot dilute sulphuric acid likewise dissolves it under disengagement of hydrogen gas, and the solution contains sulphate of protoxyde of tin. When a current of *chlorine gas* is passed over heated tin, liquid perchloride of tin is obtained. Tin is also dissolved by digestion in a solution of pure *potash*. At a high temperature it decomposes water, and is converted into peroxyde of tin, hydrogen being disengaged.

24. GOLD, Au.

(*Or.*)

* Gold has a yellow characteristic colour, which is not altered by exposure in the air. Reduced into extremely thin leaves it has a green colour, when viewed through transmitted light. When precipitated in the state of very fine powder it is brown, but its metallic lustre and yellow colour can be restored by friction. It is one of the heaviest metals, its specific gravity

being from 19·2 to 19·4. It is soft, and very ductile. It may be rendered hard by hammering, but its softness is restored by exposure to a red heat, a phenomenon which several metals have in common. A somewhat high temperature is requisite to fuse it, which must be stronger than for silver, or even for copper. The strongest heat that can be produced does not volatilise it[1], and it is not oxydised by being heated in contact with the air.

* Gold, even in the finest state of division, is insoluble in nitric, in muriatic, and in sulphuric acids. Its only solvent is aqua regia: the solution contains perchloride of gold, and imparts a purple colour to the human skin. Gold at a high temperature does not decompose water.

25. PLATINUM, Pl.

(*Platine.*)

* Platinum is of a light steel-grey colour. In the state of fine powder it is grey, and devoid of metallic lustre; yet if spongy platinum be at all rubbed with a hard body, it immediately becomes brilliant. Its specific gravity is greater than that of any other metal; it varies from 21·4 to 21·7; it is harder than copper, and ductile; but less so than gold and silver. It cannot be fused in any furnace; but when the extremity of a platinum wire is heated in the flame of a spirit-lamp, urged upon it by a stream of oxygen gas, it may be fused[2]. It is not oxydised by exposure to a red heat in the air.

* Platinum, even when finely divided, is altogether insoluble

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[1] When, however, fused in the focus of an ardent mirror, it is gradually volatilised, and a piece of silver held a few inches above it may be gilt by its fumes. When fused, gold contracts in cooling more than any other metal, and could not be used for casting. The colour of gold becomes paler by fusion with borax, but the original colour may be restored by fusion with nitre or common salt.—Ed.

[2] It may be fused also most readily by the oxyhydrogen blow-pipe, and even by an inflamed jet of a mixture of atmospheric air and hydrogen. At a very high temperature, produced by a good furnace, platinum becomes soft, and agglomerates like iron, so that it can then be welded.—Ed.

in all acids except aqua regia, and even then heat must be applied, and much more difficultly than is the case with gold. The solution contains perchloride of platinum. When platinum is combined with certain metals, for example, with silver, nitric acid may dissolve a small quantity of it. It is attacked and incompletely oxydised by fusion with the pure alkalies, and with nitrate of potash. It does not decompose water at any temperature.

26. OSMIUM, O.

(*Osmium.*)

* OSMIUM in the compact state has a metallic lustre. Ordinarily it is obtained only in the form of a porous powder, in which case it is black, without metallic brilliancy, though it may acquire it by friction with a hard body. Its specific gravity is less than that of silver, being about 10. When heated in closed vessels it does not undergo any change; but as soon as it is heated in the air, it immediately emits the characteristic disagreeable odour of osmic acid, into which it is very easily converted. When in a fine state of division, it may be ignited in the air, and it then continues to be red hot[1]. According to Berzelius, this phenomenon does not take place when the metal is more cohesive, in which case the ignition ceases as soon as the fire is withdrawn. It is not oxydised at the ordinary temperature of the air, and even at 100° cent. (212° Fahr.) it does not yet emit the characteristic smell of osmic acid.

* Osmium is dissolved by nitric acid, by which it is converted into osmic acid; but the solution is slow. When the liquor is heated, the two substances evaporate together. Osmium is more easily dissolved by aqua regia, but this is probably owing to the greater concentration of the acid; since osmic acid only is produced, and not chloride of osmium. Fuming nitric acid is of all re-agents that which dissolves osmium best, especially with the help of heat. When, however, the metal has been exposed to a very high temperature in closed vessels, it is no longer soluble in

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[1] The result of this combustion is osmic acid, and no residuum is left.—ED.

acids. In order to restore its solubility, it is necessary to fuse it with nitrate of potash in a porcelain retort, provided with a receiver, to which a tube is adapted, plunging in dilute ammonia. This retort must be gradually brought to a white heat. Part of the osmic acid which is formed is then volatilised, and dissolved in the ammonia; another portion combines with the potash, and remains in the retort. The residuum being now dissolved by water, and nitric or muriatic acid poured in the liquor, the osmic acid may be obtained by distillation. When chlorine gas is passed over osmium, the metal is not altered at the ordinary temperature; but when the metal is heated, a portion is converted into green protochloride of osmium, and another into red perchloride of osmium. These two chlorides are volatile, yet the former more so than the latter. When steam of water is projected upon osmium exposed to a high temperature, it (the steam) is slightly decomposed, according to Regnault, but as the decomposition very soon ceases, it is uncertain whether it is caused by the osmium or by any foreign substances mixed with it.

27. IRIDIUM, Ir.

(Iridium.)

* METALLIC iridium has exactly the appearance of platinum, except that it is brittle and easily reduced to powder[1]. It is very heavy, though less so than platinum and gold, its specific gravity being 18·68. The strongest heat that can be produced is ineffectual in fusing it; a temperature which determines the fusion of platinum does not even round the edges of a piece of iridium. When very finely divided, it becomes oxydised when left to cool in the air, and is converted into oxyde of iridium (IrO_3). When in more compact masses it is less easily oxydised. The oxyde

retains its oxygen at a red heat, but it is reduced without any addition by augmenting the temperature. If a piece of metallic iridium be introduced in the flame of a spirit-lamp, it very soon becomes covered with a vegetation of charcoal similar to that which is formed on the wick of a candle which wants snuffing.

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[1] This of course refers only to the iridium obtained by reduction from the oxyde of the metal, by the calcination of a double chloride with carbonate of potash, washing the mass with water, and then with muriatic acid, pressing strongly whilst yet damp, drying it, and reducing by a strong heat, by which means a cohesive mass may be obtained, which will bear polishing, but which is reduced to powder by hammering.—ED.

* Iridium is insoluble in nitric acid, in muriatic acid, in dilute sulphuric acid, and even in aqua regia. When combined with a large quantity of platinum, it is slightly soluble in aqua regia. When fused with bisulphate of potash, it is converted into sesquioxyde of iridium (Ir_2O_3), but does not dissolve. The same effect is produced when strongly heated in the air with pure potash or carbonate of potash. It is likewise converted into sesquioxyde of iridium when heated with nitrate of potash, but in that case the presence of the air is not necessary. Iridium is converted into bichloride of iridium (*chlorure iridique*, $Ir\,Cl_2$), when, after being reduced into fine powder, it is carefully mixed with chloride of potassium or of sodium, and the mixture exposed, when it begins to be red hot, to the action of a current of chlorine gas.

* Iridium forms with osmium a natural alloy, in which the two metals are so intimately combined, that the osmium cannot be dissolved by either nitric acid or aqua regia. The osmium is not even oxydised when the alloy is heated in contact with the air, or in oxygen gas, so that its presence cannot be detected by the odour of osmic acid. Neither is the alloy attacked by heating it in chlorine gas. The alloy can be decomposed only by fusing it with carbonate of potash, because the two metals are then oxydised, and after decomposition they may be separated from each other by following the process which will be described in the second part of this work.

* The odour of osmic acid, which is exhaled when the metal is heated in the air, is doubtless an excellent means of recognising whether the iridium obtained contains any osmium. Yet the action of gaseous osmic acid on the alcoholic flame furnishes, according to Berzelius, a more delicate and more commodious test. If a very small piece of pure osmium be placed upon a foil of

platinum, near the edge, and if the foil be introduced into the flame of burning alcohol, so as to heat the metal well, and yet so that part of the flame may freely rise above the edge, the flame which surrounds the osmium suddenly becomes extremely brilliant, like that produced by the combustion of pure bicarburetted hydrogen (*olefiant gas*). If iridium containing traces of osmium be treated in the same manner, the flame is seen immediately to become brilliant, though less so than when the experiment is tried with pure osmium; the brilliancy of the flame soon ceases, not because the osmium is already expelled, but because the two metals uniting together, form a fixed combination which is not susceptible of a higher degree of oxydisation. When the platinum foil is introduced far enough in the flame to place the combination in the interior part of the flame, it is reduced, and the metal may be again inflamed; as soon as brought to the exterior part of the flame, it becomes red hot for a moment, and the flame immediately becomes brilliant. It may afterwards be heated white hot without disengaging the odour of osmic acid, and without undergoing any further change. After a new reduction the same phenomenon may be re-produced, and so on in a distinct manner, even when by heating the reduced metal it is no longer possible to detect the formation of osmic acid by its odour.

* The action of iridium at a high temperature upon water has not been examined.

28. PALLADIUM, Pd.

(*Palladium.*)

* IN the compact state, palladium resembles platinum, but its specific gravity is much less, being only from 11·3 to 11·8. It is malleable, and as difficult to fuse as platinum. Heated in contact with the air to incipient redness, it becomes tarnished, and of a bluish colour, but this change does not extend beyond the surface, and the weight of the metal is not sensibly augmented. If it be heated more strongly, and cooled rapidly, it re-assumes its metallic state. When a piece of metallic palladium is put in the

interior flame of a spirit-lamp, it becomes covered with a pretty thick coating of a black carbonaceous powder, which is carburet of palladium. This phenomenon is always very distinct when finely-divided palladium is held in the interior flame of a spirit-lamp. If the metal be suddenly withdrawn, it soon becomes red-hot in the air for two or three minutes, that is to say, until the carbon has burnt, after which pure palladium remains.

* Palladium is soluble with the help of heat, in nitric acid, though with some difficulty, which properly distinguishes palladium from platinum. The solution contains protochloride of palladium, and has the same colour as that of platinum in aqua regia. Palladium is not dissolved by muriatic acid, nor by dilute sulphuric acid. Aqua regia dissolves it much more easily than nitric acid, yet the solution contains protochloride of palladium only. By fusion with pure potash, or with nitrate of potash, palladium is converted into protoxyde of palladium, but it is thus much less oxydised than iridium, osmium, and rhodium. When a few drops of an alcoholic solution of iodine are evaporated upon palladium foil, it becomes black, which is not the case with platinum: the two metals may thus easily and readily be distinguished from each other.

* Water is not decomposed by palladium, even at a white heat.

29. RHODIUM, R.

(Rhodium.)

* Rhodium, in the metallic state, forms a grey powder which it is impossible to fuse by the strongest heat, by which, however, it is rendered somewhat cohesive. In that state it is silver-white. Its specific gravity is 11. By exposure to a red heat in the air, it becomes oxydised, and is converted into a combination of protoxyde and peroxyde of rhodium[1]. At a higher heat the oxydised metal is reduced.

* Metallic rhodium is insoluble in nitric acid, muriatic acid, dilute sulphuric acid, and even in aqua regia. When, however,

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[1] Protoxyde of rhodium has never yet been isolated.—Ed.

it is alloyed with other metals, for example, with platinum, it is then soluble in aqua regia [1]; but if the alloy contains much rhodium, a large portion of the latter metal remains insoluble. Rhodium alloyed with gold or silver, is insoluble in aqua regia [2]. When rhodium is fused with bisulphate of potash, it becomes oxydised and dissolved. It can also be dissolved by fusion with phosphoric acid and the acid phosphates. Fused with pure potash, or with nitrate of potash, it is converted into peroxyde of rhodium. When metallic rhodium is carefully mixed with chloride of potassium or of sodium, and the mixture is heated, and if when it begins to be red hot, a current of chlorine gas be passed over it, it becomes converted into perchloride of rhodium. If the red-hot metal alone be exposed to the action of a stream of chlorine gas, the result obtained is a mixture of proto and of perchloride of rhodium.

The action of rhodium at a high temperature upon water has not been examined.

30. MERCURY, Hg.

(*Mercure.*)

* Mercury is distinct from all other metals, because at the ordinary temperature of the atmosphere it is liquid, and so much the more so, as it is purer. At a very low temperature, about 40° cent. below 0, (—40° Fahr.) it congeals, in which state it is malleable and soft; at + 360° cent. (680° Fahr.), it boils, and is reduced into vapour. Liquid mercury has the whiteness of tin; it is heavier than silver, its specific gravity being from 13·5 to 13·6.

* At the ordinary temperature of the air, mercury experiences no change. If it be kept exposed for a long time at a high temperature, which, however, must not be above its boiling point, it becomes converted into peroxyde of mercury, which, at a higher temperature still, is reduced, and again returns to the metallic state.

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[1] When alloyed with copper, bismuth, or lead, it is likewise soluble in aqua regia. —Ed.

[2] Rhodium, alloyed with silver or with gold, is insoluble in aqua regia; but then the aqua regia dissolves the gold or the silver.—Ed.

* MURIATIC ACID, even concentrated, has no action upon mercury, even with the help of heat. Cold NITRIC ACID gradually dissolves it, and converts it into nitrate of suboxyde of mercury. When *nitric acid* is boiled with an excess of mercury, nitrate of suboxyde of mercury only is formed, which crystallises as the liquor cools. When, on the contrary, there is an excess of *nitric acid*, the mercury is dissolved, and is converted into nitrate of protoxyde (pernitrate) of mercury. By boiling mercury with an excess of AQUA REGIA, it completely dissolves, and the solution contains peroxyde and perchloride of mercury. Dilute SULPHURIC ACID scarcely attacks mercury in the cold, but if the metal be boiled with concentrated sulphuric acid, it is converted into solid sulphate of peroxyde of mercury, the formation of which is accompanied by a disengagement of sulphurous acid. If only a small quantity of *sulphuric acid* be employed, and the whole be heated, but not to boiling, sulphate of suboxyde of mercury is produced. A current of chlorine gas directed upon mercury gently heated, transforms it into perchloride of mercury. Metallic mercury, on account of its volatility, cannot decompose water at a high temperature.

31. SILVER, Ag.

(*Argent.*)

* SILVER has a very white colour, and a great metallic lustre. It is very malleable and a little harder than gold, but requires for fusion a less degree of heat. In contact with the air it is not oxydised at any temperature; yet after fusion it attracts the oxygen from the air, but parts with it again on cooling. Its specific gravity is from 10·47 to 10·54.

* MURIATIC ACID, even concentrated, and though heat be applied, attacks silver only superficially, and the surface is converted into chloride of silver; the quantity of chloride of silver thus formed is always very feeble. Silver is attacked by NITRIC ACID, even in the cold, and dissolved by it; the solution contains oxyde of silver. Very dilute SULPHURIC ACID has no action upon silver, but concentrated sulphuric acid converts it

with the help of heat into sulphate of silver, under disengagement of sulphurous acid. When silver is melted with nitrate of potash, or with the pure alkalies in contact with the air, it is not oxydised, nor does it experience any alteration.

* When silver is alloyed with more than one quarter of gold, the silver, which forms part of the alloy, is not completely dissolved by nitric acid. But if this alloy be melted with more silver, so that the gold forms only one quarter part of it, then the gold and the silver may be completely separated by means of *nitric acid.*

* At a white heat silver may decompose water, with disengagement of hydrogen gas; it absorbs the oxygen of the water, but it abandons it on cooling, and metallic silver remains.

32. COPPER, Cu.

(*Cuivre.*)

* COPPER has a red colour, which is characteristic, and much metallic lustre. It is very malleable, and harder but lighter than silver. Its specific gravity is from 8·66 to 8·72. It fuses at about the same temperature as gold, but somewhat lower. At the ordinary temperature it is not sensibly altered by a dry atmosphere; and when in contact at the same time with air and water, the oxydisation produced is very slight. Heated red hot, in contact with the air, it is oxydised; it becomes then covered with a black crust of protoxyde of copper, which on cooling may be easily detached.

* Pure metallic copper is insoluble in MURIATIC ACID out of the contact of the air, even with the help of heat, which, however, dissolves a slight portion of it when the experiment is performed in the open air; ordinarily, the solution then contains subchloride of copper. Copper is easily dissolved by NITRIC ACID; the solution contains protoxyde of copper. Very dilute SULPHURIC ACID does not attack copper, but concentrated *sulphuric acid* converts it, with the help of heat, into sulphate of protoxyde of copper, the formation of which is accompanied by a disengagement of sulphurous acid. Copper, heated in

an atmosphere of CHLORINE GAS, is converted into a mixture of subchloride and of protochloride of copper.

* At a white heat, copper decomposes water with disengagement of hydrogen gas, and formation of protoxyde of copper; but the decomposition is very weak and slow.

33. URANIUM, U.

(*Uranium.*)

* METALLIC URANIUM is but little known. According to Arfwedson, when obtained by reducing the sesquioxyde of uranium by means of hydrogen gas, it forms a powder of a cinnamon-colour, which has no metallic lustre. When it has been obtained by reduction from the potassio-chloride of uranium by hydrogen gas, it may be obtained in octahedral crystals of a dark grey colour, and with a metallic brilliancy, which, when examined by daylight with a magnifying-glass, appear transparent, and of a dark-brown colour.

* Uranium is insoluble both in MURIATIC and in SULPHURIC ACIDS, even when concentrated. NITRIC ACID, on the contrary, dissolves it easily, and the solution contains sesquioxyde of uranium.

* At a dark-red heat, metallic uranium decomposes water, with disengagement of hydrogen gas, and formation of protoxyde of uranium; but the decomposition is very slow.

To the French edition the following remarks have been added by E. Peligot:—

"The above-described properties belong to protoxyde of uranium (U O); it is known that until lately the latter compound had been mistaken for the metal. By treating a mixture of this oxyde and of charcoal at a red heat by chlorine gas, carbonic oxyde and a volatile chloride of uranium are obtained, which being decomposed by potassium, yields metallic uranium."

* " Uranium thus prepared forms a black powder, which may

be kept in contact with the air for some considerable time without being oxydised; but when heated it burns with a light which is remarkable for its brilliancy and whiteness. A few particles of this metal are sufficient to characterise it, for by projecting them in the flame of a wax-candle, brilliant sparks are thus produced which no other metal can form under the same circumstances."

* "Uranium, at the ordinary temperature, does not decompose water; it dissolves in the dilute acid with disengagement of hydrogen; the solutions are green when the acid has not acted as an oxydising agent, and possess the properties which were attributed to the salts of protoxyde of uranium."

* "With NITRIC ACID a yellow solution of nitrate of peroxyde of uranium is obtained."

* "This metal combines with chlorine with disengagement of heat and light, and the product is a green protochloride of uranium."

* "It combines likewise with sulphur with disengagement of light."

34. BISMUTH, Bi.

(Bismuth.)

* METALLIC bismuth is of a reddish silver-white colour; this reddish tinge distinguishes it from antimony, which it very much resembles with respect to its very lamellar structure, its fragility, and the ease with which it may be pulverised. It is more fusible than lead, and may be volatilised in close vessels, although a very great heat is necessary to effect this. It is not altered by exposure to either damp or dry air. In contact with water it becomes here and there slowly converted into oxyde and into hydrate of bismuth; the rest of the surface of the metal presents a reddish-brown, and then a violet-blue colour. Heated to fusion in the open air, it becomes covered with a grey pellicle of oxyde of bismuth. At a white heat, it ignites, and burns with a bluish-white flame, and becomes converted into oxyde of bismuth. When a small piece of bismuth

is heated upon charcoal by means of the blow-pipe, the charcoal receives a yellow coating of oxyde of bismuth. The specific gravity of bismuth is 9·83.

* Bismuth, heated with MURIATIC ACID, is dissolved by it, but with great difficulty, and sparingly, hydrogen being disengaged at the same time. This metal is soluble in NITRIC ACID at the ordinary temperature, and the solution contains oxyde of bismuth. When pulverised bismuth is treated by fuming *nitric acid*, the reaction is so violent that the metal becomes red hot. SULPHURIC ACID acts upon bismuth, but the help of heat is necessary, and it must be concentrated; it is thus converted into sulphate of bismuth with disengagement of sulphurous acid. A current of CHLORINE gas passed over heated bismuth converts it into chloride of bismuth, which, at a high temperature, is volatile. At a white heat bismuth decomposes water with disengagement of hydrogen gas, and formation of a little oxyde of bismuth, but the decomposition is very slow.

35. LEAD, Pb.

(*Plomb.*)

* LEAD has a grey colour and much brilliancy; it stains paper, and is very soft. Its specific gravity is 11·445; it is therefore heavier than silver: it begins to fuse at about +280° cent. (536° Fahr.); heated in contact with the air it begins to volatilise at a low red heat, but in closed vessels a white heat is required to volatilise it. It is not altered by exposure to dry air, but in damp atmosphere it becomes slightly oxydised, its surface becomes dull, grey, and sometimes iridescent. Plunged in distilled water with the contact of the air, but sheltered from the influence of carbonic acid, white spangles of hydrate of lead only are produced according to Bonsdorff. To obtain this effect, however, it is necessary that the water should be perfectly pure, for the least quantity of salts or of foreign substances prevents the formation of the hydrate. The nitrates form the only exception, for their presence does not prevent the formation of the hydrate of lead, unless they be in very large quantity;

wherefore metallic lead may be resorted to as a test of the purity of water. In effect, when fine recently-prepared lead filings are thrown into a tumbler full of water, in two or three minutes a small cloud of hydrate of lead will appear if the water be pure; whilst, in the contrary case, no turbidness is produced. If metallic lead be put in contact with water and with ordinary atmospheric air containing carbonic acid, a little hydrate of lead is at first formed, but a combination of hydrated carbonate of lead is soon deposited in the form of thin white spangles, having a waxy appearance. If metallic lead be left in contact with air and water for several months, or for several years, deutoxyde of lead may be formed.

* When lead is heated in the air, but not so strongly as to fuse it, it becomes covered with a black pellicle; and if heated in the air until it fuses, the above pellicle assumes a brownish-yellow colour.

* Lead is insoluble in cold MURIATIC ACID, and even with the application of heat it is but little attacked. It is completely dissolved by NITRIC ACID; the solution contains protoxyde of lead. SULPHURIC ACID acts upon lead only with the help of heat, and in the concentrated state, by which it is converted into sulphate of lead. When lead is heated in chlorine gas, it becomes transformed into chloride of lead. At a white heat, lead decomposes water, though slowly, hydrogen gas being disengaged and protoxyde of lead formed.

36. CADMIUM, Cd.

(*Cadmium.*)

* THE colour of cadmium resembles that of tin, and has much brilliancy. It is soft, flexible, and produces a creaking noise, like tin when bent. It is very fusible, and melts below incipient redness. It boils and evaporates at a temperature slightly superior to that of boiling mercury. At the ordinary temperature it is not much altered by dry air, and a damp atmosphere only slightly impairs its brilliancy; in aërated water, it becomes coated with hydrated oxyde of cadmium, which, in

course of time, absorbs carbonic acid. Heated in the air, it burns and emits brownish-yellow fumes of oxyde of cadmium. Its specific gravity is 8·6.

* Cadmium is soluble in MURIATIC ACID, provided it be not too dilute, and produces a disengagement of hydrogen gas, especially with the help of heat. It is dissolved by NITRIC ACID more easily than by any other acid. Dilute SULPHURIC and other strong acids, even ACETIC ACID, dissolve cadmium, with disengagement of hydrogen gas; the solution, however, is slowly effected. Cadmium, at a low red heat, easily decomposes water, with disengagement of hydrogen gas and formation of oxyde of cadmium. On account, however, of the volatility of this metal, it must be reduced to the state of vapour before putting it in contact with the aqueous steam.

37. NICKEL, Ni.

(*Nickel.*)

* NICKEL in the melted state is silver-white, with a slight tinge of grey, with metallic brilliancy. In the extremely divided state in which it is obtained, by reducing its oxyde by means of hydrogen gas, or by exposing the oxalate of nickel to a red heat, it forms a greyish-black powder. This metal is very hard; it is malleable and difficult to fuse. It is distinguished from the other metals, because it may be rendered magnetic, and retains the magnetic power. At the ordinary temperature it is not at all altered by atmospheric air. Heated in the open air it is oxydised; yet the oxyde of nickel may be reduced without addition, when exposed to a very high temperature in a charcoal fire, because it is then reduced by the carbonic oxyde gas which is produced. Its specific gravity is 8·3.

* Nickel is dissolved by MURIATIC ACID when not too dilute, especially with the help of heat, hydrogen gas being disengaged; the solution is slowly effected, and the liquor contains chloride of nickel. Nickel is easily dissolved by NITRIC ACID. Dilute SULPHURIC ACID dissolves it somewhat

difficultly, with the help of heat, under disengagement of hydrogen gas. The solutions of nickel in the acids, even in *aqua regia*, contain oxyde and chloride of nickel, and they are green. When finely divided nickel is heated in an atmosphere of chlorine gas, a vivid ignition is manifested, and chloride of nickel is produced, which forms yellow crystalline spangles, soft to the touch like mica, and which at first appear to be insoluble in water; but when left exposed to the air for a long time they become green, and they are then soluble in water.

* At a low red heat nickel decomposes water but slowly; hydrogen gas is disengaged, and oxyde of nickel formed.

38. COBALT, Co.

(*Cobalt.*)

* METALLIC cobalt is grey with a reddish tinge; reduced into very fine particles it has a greyish-black colour. It is slightly ductile, and the presence of a small quantity of arsenic or of carbon renders it brittle. It is less fusible than gold. It differs from most other metals, because it is attracted by the magnet, though less than iron and nickel, and, like them, retains the magnetic power. It is not altered by exposure to the air at the ordinary temperature; but at a red heat it is slowly oxydised. Its specific gravity is about 8·0.

* Cobalt is slowly dissolved by MURIATIC ACID under disengagement of hydrogen, and better with the help of heat, and with a concentrated acid. Cobalt is easily dissolved by NITRIC ACID. It is dissolved also by dilute SULPHURIC ACID, with the help of heat, hydrogen being disengaged; and by *concentrated sulphuric acid*, with disengagement of sulphurous acid. The acid solutions of cobalt, even that in AQUA REGIA, contain chloride and oxyde of cobalt; they are red, though when very concentrated their colour is blue, especially if they contain a free acid. The blue solutions become red by addition of water. When a current of chlorine gas is passed upon finely divided cobalt, the latter being heated, it ignites, and is converted into blue crystalline spangles of chloride of cobalt.

* Cobalt easily decomposes water at a red heat, and with disengagement of hydrogen and formation of oxyde of cobalt.

39. ZINC, Z.

(*Zinc.*)

* METALLIC zinc is white with a bluish tinge; it is very bright, and of a lamellar texture. It is slightly flexible, and may even be reduced into pretty thin sheets, especially when very pure. The ordinary and impure zinc of commerce[1] is flexible, and can be laminated only at a high temperature, which, however, should not exceed that of boiling water[2]. It fuses at about + 360° cent. (680° Fahr.), and at a white heat it boils, and may be distilled. It is not altered by exposure to dry air. Put in contact with water and atmospheric air containing carbonic acid, it is first converted into hydrate of oxyde of zinc, which absorbs carbonic acid, and combines with it. In water from which the air has been expelled, it may be preserved for years without losing its lustre. Exposed to a high temperature in the open air, it burns with a dazzling greenish-blue light, and emits thick white fumes of oxyde of zinc. Its specific gravity is 6·86.

* Zinc is easily dissolved by muriatic acid, even at the ordinary temperature, and hydrogen gas is copiously evolved. It is likewise easily dissolved by nitric acid. *Sulphuric* acid dissolves it very promptly, even in the cold, hydrogen being disengaged[3].

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[1] The zinc of commerce is generally contaminated with iron, lead, arsenic, copper and carbon; the zinc manufactured by what is called the Belgian process generally contains a large proportion of iron, which it absorbs whilst remaining in the fluid state in the cast-iron nozzles placed at the end of the retorts, and in which the volatilised zinc is condensed. The presence of iron renders the zinc brittle; and I have ascertained that three per cent. of iron is sufficient to make the zinc crumble into powder under the hammer; on the other hand, zinc which contains five per cent. of iron is unfit for zincing iron plates, chains, &c.—ED.

[2] Zinc is generally heated to about 250° Fahr. before laminating.—ED.

[3] Pure zinc is scarcely acted upon by sulphuric acid, but the slightest quantity of foreign metal immediately causes it to dissolve with effervescence. Sulphuric acid, which is, as just said, almost without action upon pure zinc, begins at once to dissolve this same zinc, if only re-melted in an iron ladle previously to subjecting it to the action of the acid. The ease with which zinc may be dissolved by sulphuric acid is, however, no proof of its being impure, that is, of its containing other metals, such

Almost all the acids which are soluble in water act in the same manner, provided they be not too much diluted. Zinc is slowly dissolved even by the solutions of pure potash, or of ammonia, under disengagement of hydrogen gas. All these solutions contain oxyde or chloride of zinc. The zinc of commerce is more easily dissolved by all the re-agents than pure distilled zinc. This metal, heated in an atmosphere of gaseous chlorine, is converted into chloride of zinc, which is volatile at a somewhat high temperature (bright red heat). At a red heat zinc decomposes water very easily, hydrogen gas is disengaged, and a very brilliant crystallised oxyde of zinc is formed.

40. IRON, Fe.

(Fer.)

* Iron is of a light-grey colour. When perfectly pure it is white. Its combination with carbon (cast iron) has a darker or lighter hue; the variety which contains only a small quantity of carbon (steel), has a lighter colour than ordinary iron (bar-iron), which is almost pure, as it contains only a feeble trace of carbon. Iron has much brilliancy, is hard and malleable. Steel is harder than iron, especially when after having been heated it is suddenly cooled. Cast-iron is hard and brittle, especially white cast-iron. Grey cast-iron is less so. All the varieties of iron are attracted by the magnet, but, properly speaking, steel is the only form which retains the magnetic power. This property distinguishes iron from all the other metals, except nickel and cobalt. Iron is very difficult to fuse. Steel is more fusible than bar-iron, and cast-iron more so than steel. At the ordinary temperature, dry air has no action upon iron, and even a damp air does not destroy its brilliancy. According to Bonsdorff, the rust or hydrate of peroxyde of iron with which it becomes covered in inhabited situations and other places,

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as iron or lead, and may be dependent on the disposition of its molecules, M. Mahier having observed that the purest zinc may be rendered easily soluble in sulphuric acid by hammering, pounding, or laminating.—Ed.

depends on the inequalities and fissures of its surface, which become oxydised, and upon which the aqueous vapour being deposited, determines the formation of the hydrate. When the iron is covered with a slight coat of black oxyde, the production of the hydrate in question is very soon induced[1].

* When iron is heated red-hot in the open air, it becomes oxydised, and covered with a crust, which is a combination of proto and of peroxyde of iron. If it be heated white-hot, either in air or in oxygen gas, it burns with beautiful sparks. The burnt or fused iron, consists then of a mixture of both the oxydes just mentioned. The specific gravity of bar-iron is 7·7.

* Iron is easily dissolved by MURIATIC ACID, under disengagement of hydrogen gas; the solution contains protochloride of iron. The hydrogen gas which is disengaged by the action of muriatic acid upon iron which contains carbon, has a disagreeable odour, and after the solution of such a piece of iron, a carbonaceous residuum is left. All the various species of iron are easily dissolved by NITRIC ACID. When iron is dissolved in cold dilute nitric acid, the solution contains protoxyde of iron. When, on the contrary, the acid employed is heated, the solution contains peroxyde of iron. After the solution in nitric acid of a piece of iron containing carbon, there remains a brown and pasty residuum, and in such cases nitric oxyde gas mixed with carbonic acid gas are evolved whilst the iron is dissolving. CONCENTRATED SULPHURIC ACID converts iron, with the help of heat, into sulphate of peroxyde of iron, sulphurous acid being disengaged. Iron is easily dissolved by cold dilute sulphuric acid, hydrogen being disengaged, and the solution contains sulphate of protoxyde of iron. When the iron dissolved in dilute *sulphuric* acid contains carbon, the hydrogen gas disengaged has a fetid odour, and a black residuum is left. Almost all the acids which are soluble in water behave like dilute sulphuric acid. The residuum which is left by iron containing carbon after treatment by an acid often contains silicic acid. When a

stream of chlorine gas is passed over heated iron, the metal is converted into perchloride of iron, susceptible of being sublimed [of course, provided a sufficient quantity of chlorine gas be employed.]

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[1] Iron rust is a mixture of carbonate of protoxyde of iron and hydrate of peroxyde of iron.—ED.

* At a low red heat, iron very easily decomposes water, hydrogen being disengaged, and magnetic ferrosoferric oxyde formed.

41. MANGANESE, Mn.

(*Manganèse.*)

* METALLIC manganese is of a greyish-white colour, and has not much lustre. It is brittle, may be easily pulverised, is less hard than cast-iron, and very difficult to fuse: its specific gravity is about 8·0. Exposed to the air, it begins to oxydise at the ordinary temperature, and falls into a black powder. In water it slowly oxydises at the ordinary temperature under disengagement of hydrogen gas; but when this liquid is heated, the disengagement of hydrogen is very rapid. It is rapidly dissolved by the aqueous acids under disengagement of hydrogen gas; that solution contains protoxyde of manganese, or if muriatic acid has been employed, the solution contains protochloride of manganese. Nitric acid dissolves manganese, but instead of hydrogen being disengaged, it is nitric oxyde gas, and the solution contains protoxyde of manganese.

42. ZIRCONIUM, Zr.

(*Zirconium.*)

* ZIRCONIUM has as yet been obtained only by Berzelius. It is a black powder, which acquires a brilliant dark iron-grey colour by friction with a burnisher. Exposed to a red heat in vacuo or in an atmosphere of hydrogen gas, it is not altered nor fused. Heated in the open air, it ignites much below red heat, and is converted into white zirconia. Before being heated red hot it becomes divided in water into such fine particles as to pass through the filter; the addition of a little muriatic acid or the solutions of salts prevent this effect.

* Zirconium is not attacked at the ordinary temperature by MURIATIC nor by CONCENTRATED SULPHURIC ACID; even with the help of heat their action is but slight, and a little hydrogen gas is disengaged. Neither is it attacked by NITRIC ACID nor by AQUA REGIA; on the contrary, HYDROFLUORIC ACID dissolves it, with the help of heat, under disengagement of hydrogen gas. A mixture of HYDROFLUORIC and NITRIC ACIDS dissolves zirconium with much violence. The solutions of the ALKALIES have no action upon zirconium, even when boiled with it. When zirconium is mixed with CARBONATE of potash, and the mixture is heated, the zirconium burns at the expense of the carbonic acid with a feeble light. When fused with the pure ALKALIES, it is oxydised at the expense of their water. Lastly, when fused with NITRATE OF POTASH or with CHLORATE OF POTASH, it begins to burn only at an incipient red heat.

43. CERIUM, Ce.

(*Cerium.*)

* ACCORDING to Mosander, cerium is a chocolate-brown powder, which slowly oxydises when exposed to damp air, and which on this account always exhales the odour of hydrogen gas. In water it oxydises, and hydrogen is disengaged; but the greater the quantity which has thus oxydised, the slower does the decomposition of the water become. At the temperature of 90° cent. (194° Fahr.) it dissolves in water as violently as if an acid had been added. By friction it acquires a slight steel-grey brilliancy: heated in the air it ignites before it has become red hot, burns vividly, and passes into the state of sesquioxyde of cerium. With chlorate and nitrate of potash it detonates.

44. YTTRIUM, Y.

(*Yttrium.*)

* ACCORDING to Wöhler, yttrium has the following properties. It forms spangles with a metallic lustre, which by washing yield a bright powder of an iron colour. It is not oxydised by

either air or water (at the ordinary temperature). When heated, it ignites at incipient redness, and is converted into white yttria. If the combustion takes place in oxygen gas, the deflagration is exceedingly brilliant. Yttrium dissolves in the dilute acids under disengagement of hydrogen gas. It is dissolved, but with difficulty, by a solution of potash, and it is altogether insoluble in ammonia.

45. THORINUM, Th.

(*Thorinum.*)

* ACCORDING to Berzelius, thorinum is a heavy metallic powder of a dark lead-grey colour. It may be compressed by means of a polished agathe burnisher, and it then acquires a metallic lustre and an iron-grey colour. If gently heated, it ignites and burns with an extremely bright flame. If small grains of thorinum be projected into the flame of a spirit-lamp they burn with a white flame, and at the moment of their combustion they appear considerably to increase in bulk; after combustion the snow-white residuum of thorina remains, but which does not present the slightest trace of fusion or of agglomeration.

* Thorinum is not oxydised by water either in the cold or with the help of heat. It is very slowly dissolved by sulphuric acid, and with disengagement of hydrogen, but ultimately the solution is complete. Nitric acid has perhaps still less action upon it. It is easily dissolved by muriatic acid with disengagement of hydrogen, and with the help of heat it is thus speedily dissolved. It is about as little acted upon by hydrofluoric acid as by sulphuric acid.

46. GLUCINIUM, Be.

(*Glucinium.*)

* ACCORDING to Wöhler, glucinium is a dark-grey powder which, at the ordinary temperature, is not oxydised in the air, nor in either cold or boiling water; but when exposed to a red heat it ignites and burns very vividly: its combustion in oxygen

gas is extremely brilliant. Hot concentrated sulphuric acid dissolves glucinium with disengagement of sulphurous acid, and in the dilute acids or in a solution of potash with disengagement of hydrogen gas. It is dissolved by nitric acid with disengagement of nitric oxyde: it is absolutely insoluble in ammonia.

47. ALUMINIUM, Al.

(*Aluminium.*)

* Aluminium, according to Wöhler, resembles pulverulent platinum; it easily acquires a perfect metallic lustre, and a tin-white colour by friction with the burnisher. It is neither fused nor agglomerated by a heat which readily fuses cast-iron. Exposed to a red heat in the open air it ignites, and burns with much brilliancy, and is converted into white and hard alumina. Its combustion in oxygen gas is so dazzling, that the eye can hardly bear it. It is not oxydised by water at the ordinary temperature; but at a boiling temperature it becomes slowly oxydised under a feeble disengagement of hydrogen gas. At the ordinary temperature it resists the action of concentrated nitric and sulphuric acids; but if heat be at all applied, it is then dissolved with violence. The dilute acids dissolve it rapidly with disengagement of hydrogen. This is also the case when it is treated by the solutions of the fixed alkalies, even when dilute. It is likewise dissolved by ammonia, hydrogen being disengaged at the same time: this alkali contains then a pretty large quantity of alumina, which is remarkable, alumina being otherwise insoluble in ammonia.

48. MAGNESIUM, Mg.

(*Magnesium.*)

* According to Bussy, magnesium has a silver-white colour, is very brilliant, hard, malleable. It may be flattened under the hammer. According to Liebig, it fuses at about the same temperature as silver. At the ordinary temperature, dry atmospheric air has no action upon it, but it is tarnished by exposure to damp air. It is not oxydised by pure water. It

burns both in oxygen and in the air, at the temperature at which glass softens; it then emits a vivid light, and is converted into magnesia. It is dissolved in the cold by the dilute acids, hydrogen being disengaged. Nitric acid, whilst dissolving it, evolves nitrogen, and concentrated sulphuric acid disengages sulphurous acid. Its acid solutions contain magnesia.

49. CALCIUM, Ca.

(Calcium.)

* CALCIUM is silver-white, and solid. It is rapidly oxydised by exposure to damp air. At the ordinary temperature this oxydisation is not accompanied by a disengagement of light; but if heat be applied it deflagrates. It is converted into lime (oxyde of calcium) by water, and dissolves in it.

50. STRONTIUM, Sr.

(Strontium.)

* STRONTIUM has been obtained only by Sir H. Davy. Its external qualities and properties resemble those of barium.

51. BARIUM, Ba.

(Barium.)

* BARIUM resembles silver. It is heavier than concentrated sulphuric acid, and malleable. It fuses before incipient redness. By exposure to damp air it is oxydised, and becomes coated with a white crust. Heated in the open air, it burns with a deep-red flame. It is oxydised by water and by the acids, with a violent disengagement of hydrogen gas.

52. LITHIUM, L.

(Lithium.)

* METALLIC lithium is very little known. It is said to resemble sodium much.

53. SODIUM, Na.

(*Sodium.*)

* SODIUM is silver-white, and has much metallic lustre. It may be pulverised at a temperature below freezing, but a slight elevation of temperature renders it malleable again. At the ordinary temperature it is soft, like wax, and fuses at a few degrees above the boiling point of water. At a low red heat it volatilises. This metal is lighter than water. According to Bonsdorff, it is not oxydised by dry air; but by exposure to damp air, it becomes coated with a crust of hydrate of oxyde of sodium. Sodium is inflamed by exposure to a red heat. It is oxydised by pure water with disengagement of hydrogen gas, but without emitting light. If, however, a little gum-arabic be dissolved in the water, the small piece of sodium remaining longer on one point, becomes hot enough to ignite, and it then burns with a yellow flame.[1] When sodium is thrown upon mercury it is violently projected with an explosion, accompanied with heat and light.

54. POTASSIUM, K.

(*Potassium.*)

* THE external qualities of potassium resemble mercury; it has almost the same colour, and is nearly as bright[2]. Yet, at the ordinary temperature it is only semi-fluid. Between 50° and 60° cent. (122° and 140° Fahr.) it becomes completely liquid. At 32° Fahr. it is solid and brittle. At a low red heat it is volatile, and may be distilled; yet it is somewhat less volatile

than sodium. It is lighter than water and than sodium. By exposure to damp air it is gradually oxydised, but more rapidly than sodium, yet without being ignited; but when heated in contact with the air it ignites, and burns with much violence. In the dry air it retains its metallic lustre. It is more powerfully oxydised by water than sodium, and hydrogen gas is disengaged. When thrown upon water, it runs about its surface, and the hydrogen which is disengaged burns with a violet or red flame. Potassium ignites spontaneously, even when thrown upon ice. When thrown upon mercury it quietly amalgamates with it, provided the air and the mercury be dry,—a circumstance which distinguishes it from sodium. But in the open air, it runs at the surface of the mercury, on account of the moisture contained in the atmosphere, and by reason of the hydrogen gas which is then disengaged.

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[1] If sodium be thrown in a dish containing only a small quantity of water, so that it may touch the dish; or if when thrown into a body of water it be struck smartly, it then ignites also and burns with a characteristic yellow flame.—ED.

[2] Potassium is now so well known that the above definition may be deemed sufficient, yet as it stands, it can hardly be called correct. Potassium at the ordinary temperature is as soft as tallow, and becomes fluid only at + 55° cent., a temperature at which it may then be compared to mercury, inasmuch as it may then be separated by pressure into small globules, which run like mercury, and like the latter coalesce with one another, when they come in contact, to form larger ones, &c.—ED.

SECOND PART.

RULES TO BE OBSERVED IN QUALITATIVE ANALYSIS.

* WHEN the object of a chemical analysis is to determine all the constituent principles contained in a substance, it is possible, by means of a few experiments performed without any particular order, to detect promptly one or the other of these principles; but it is generally advantageous to follow a systematic course, for in qualitative analysis nothing is more frequent or easy than, by neglecting apparent minutiæ, to commit grave errors, and to overlook the presence of several of the substances which may nevertheless be contained in the compound under examination.

* Before describing the course to be followed for the detection of the constituent principles of compound combinations, it is necessary to speak first of the re-agents employed to obtain this result, and of the manner of using them.

CHAPTER I.

RE-AGENTS.

* THE number of the re-agents employed in qualitative analysis of compounds which contain only substances of frequent occurrence is not considerable. Those chiefly used are the following:—

1. MURIATIC ACID.

(*Acide Chlorhydrique.*)

* THIS is the most indispensable of all the acids used in chemical analysis. It is not only a test for oxyde of silver (page 129), suboxyde of mercury (page 134), and oxyde of lead (page 99); but it is also principally used as a solvent of most of the oxydised substances which are insoluble in water. It is also used in preference to any other for the purpose of rendering acid a neutral or an alkaline solution; it is seldom only that it is better to employ another acid for the purpose. It is also employed for detecting carbonic acid. Muriatic acid is also to be preferred to other volatile acids for the detection of free ammonia in solutions (page 22). Lastly, it is employed for the detection of certain peroxydes and of some acids the oxygen of which has not much affinity for the radical, in which case a disengagement of chlorine gas is evolved.

* *Muriatic acid* DISSOLVES only those metals which decompose water with the help of an acid under disengagement of hydrogen, such as zinc, iron, &c.

* Diluted with water it likewise dissolves several metallic sulphurets with disengagement of sulphuretted hydrogen.

* The metallic phosphurets are not soluble in it. Almost all oxydes are dissolved by *muriatic acid,* at least when they have not been previously ignited.

* The oxydes which form bases are generally more soluble in it than those which behave like an acid. Among the first, the only exceptions are *oxyde of silver, suboxyde of mercury,* and *oxyde of lead,* because their corresponding chlorides are either sparingly soluble or altogether insoluble. *Muriatic acid* is especially employed to dissolve the oxydes which are insoluble in water; and it is only in a few particular cases that another acid is resorted to for the purpose. Most oxydes, after ignition, are less soluble in muriatic acid than before; a few become thus altogether insoluble in it; such is the case with *peroxyde of tin, oxyde of chromium,* and pure *titanic acid.* The oxysalts which are insoluble in water are for the most part soluble in muriatic acid; the salts of the *above three oxydes* must, however, be excepted, and likewise the *sulphates* and *seleniates* of *baryta,* of *strontia,* of *lime,* and a few others.

* When the acids which the salts contain are not soluble in muriatic acid, it often occurs that these salts undergo a decomposition, in consequence of which, the muriatic acid employed dissolves the base, and leaves the acid; such is the case, for example, with several silicates.

* Muriatic acid is, properly speaking, the solvent of the salts and of the oxydes which are insoluble in water; no other acid can be preferred in this respect, except under peculiar circumstances.

* *Muriatic acid* DOES NOT DISSOLVE the metals which are not susceptible of decomposing water with the help of an acid; many metallic sulphurets likewise resist its action; many sulphurets, however, which are not attacked by diluted muriatic acid, are decomposed by the concentrated acid, especially with the help of heat; neither can it dissolve most of the solid, simple, non-metallic substances, such as *sulphur, selenium, phosphorus, carbon;* the oxydes of the bases the chlorides of which are insoluble,

the salts of these oxydes, and a few other combinations, of which we have just been speaking, and many native silicates, cannot be dissolved by *muriatic acid.*

* Ordinarily the muriatic acid employed is moderately diluted, and of a specific gravity 1·110 or 1·120, to which more water in most cases may be added. A stronger or fuming acid is seldom called for.

* MURIATIC ACID is not fit for analytical research, except it be very pure. The impurities most frequently met with are SULPHURIC ACID, PERCHLORIDE OF IRON, ORGANIC SUBSTANCES, CHLORINE, SULPHUROUS ACID, and HYDROBROMIC ACID, ARSENIOUS ACID: the presence of sulphuric acid may be readily detected by diluting it, and testing with chloride of barium, which will produce a white precipitate of sulphate of baryta, which, however, may require some time in order to appear if the quantity of sulphuric acid be very minute. If the muriatic acid is *yellow* or *yellowish,* it is generally a proof that it contains *organic substances,* or *perchloride of iron;* the presence of the latter is detected by supersaturating the acid with ammonia, by which reddish-brown flakes of peroxyde of iron will be precipitated, either at once, or after a little time. The presence of iron may, however, be tested more sensitively by first supersaturating with ammonia as just said, and then adding hydrosulphuret of ammonia, which will produce a black precipitate of sulphuret of iron. The presence of ORGANIC SUBSTANCES is indicated by the colour of the acid, and because, if a few drops of the acid be evaporated in a watch-glass, a carbonaceous residuum is left. The presence of free CHLORINE is recognised partly by the smell, and partly because a few drops evaporated on a platinum foil leave a residuum[1]. If the quantity of free chlorine be at all considerable, the acid will dissolve gold leaf. If the muriatic

acid contains [free] SULPHUROUS ACID, its presence may often be detected by its odour, or by means of sulphuretted hydrogen [1], or of protochloride of tin [2]. Sometimes the acid contains HYDROBROMIC ACID, which may be detected by aqueous solution of chlorine and ether (page 427). Muriatic acid may also be contaminated by ARSENIOUS ACID, which is often the case when prepared by means of an arseniferous sulphuric acid, in which case sulphuretted hydrogen will produce a yellow precipitate, from which metallic arsenic may be extracted by the processes indicated before (pages 338 to 382). The presence of fixed substances, such as chloride of sodium, may be recognised by evaporating a small quantity of the acid in a watch-glass, or upon a piece of platinum foil. Sometimes, though very rarely, muriatic acid contains SELENIOUS ACID, which may be recognised by means of a sulphosalt [3].

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[1] This residuum is chloride of platinum, formed, of course, at the expense of the platinum foil, or else it may be some other fixed substance, such as oxyde of iron, or chloride of sodium, sulphate of soda, unless the absence of these substances has been ascertained before. The presence of free chlorine may likewise be readily detected by boiling the acid under examination with a few drops of sulphate of indigo, the blue colour of which will be destroyed if the acid contains a minute trace of free chlorine, and left unimpaired in the contrary case.—ED.

2. NITRIC ACID.

(Acide Nitrique.)

* NITRIC ACID is employed in certain cases for dissolving the oxydised substances which are insoluble in water, when the presence of muriatic acid must be avoided.

* Although most of the combinations which it forms with the bases are soluble, it is by no means preferable to muriatic acid as a solvent of oxydised substances; because they generally

dissolve less readily in nitric than in muriatic acid, and the excess of acid which it is then necessary to employ, is more difficult to eliminate by heat. When operating upon non-volatilisable substances, the most troublesome peculiarity attending the use of nitric acid is the expulsion of the nitrate of ammonia which is formed in large quantity when nitric acid is used instead of muriatic acid for dissolving an oxyde, and ammonia employed for supersaturating the solution thus obtained. This expulsion of the ammoniacal salt is attended with difficulties, because, in that case, when nitrate of ammonia exists in sufficient quantity along with organic substances, an explosion may often take place. *Nitric acid* is sometimes employed instead of muriatic acid, and especially for acidifying neutral or alkaline solutions; but this is seldom necessary. Nitric acid is, however, especially employed for dissolving metals and metallic alloys, because metals cannot often be dissolved except by nitric acid. It is used also for oxydising the metallic sulphurets (page 455), and to convert substances in solution into a higher degree of oxydisation; for example, protoxyde into peroxyde of iron. Ordinarily, the pure nitric acid made use of is diluted to the strength of ordinary *aqua-fortis* [1]; the cases in which fuming nitric acid containing nitrous acid is employed are rare, such as for oxydising the metallic sulphurets. Instead of nitric acid, a mixture of one part of this acid and two parts of muriatic acid (AQUA REGIA) is sometimes employed; in which case, it is of course immaterial that the nitric acid contain muriatic acid; but it must be free from *sulphuric acid*.

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[1] The result will be a milky-white precipitate of sulphur; if the precipitate be yellow, the presence of arsenious acid may be suspected, or else that of selenious acid. But, according to Messrs. Fordos and Gelis, the best method of detecting traces of sulphurous acid in muriatic acid consists in dissolving a little zinc in the acid, and in passing the hydrogen gas evolved through a solution of subacetate of lead (or, better still, through a solution of oxyde of lead in caustic potash); the sulphuretted hydrogen thus formed will precipitate sulphuret of lead, by which means the slightest trace of sulphurous acid will be rendered apparent.—ED.

[2] After a certain time, if sulphurous acid be present, the acid will assume a brown tinge, or even a brown precipitate will be formed, which is sulphuret of tin. The presence of sulphurous acid may be also detected by adding a little nitric acid, by which the sulphurous acid, being converted into sulphuric acid, may now be tested by chloride of barium.—ED.

[3] See page 231 for the detection of selenious acid. See Berzelius' Report for 1845, page 138.—ED.

* Nitric acid, especially with the help of heat, DISSOLVES nearly all the metals under disengagement of nitric oxyde, and sometimes also of nitrous acid gas. The only metals insoluble in it are gold, platinum, and some other metals mentioned before. It dissolves nearly all the oxydes, except *peroxyde of tin*, *oxyde of antimony*, *tellurious acid*, and a few others after ignition, and also the salts produced by the oxydes which are

insoluble in water. Peroxydes are partially converted by nitric acid into a basic oxyde and a higher degree of oxydisation. The simple non-metallic bodies, such as *sulphur, selenium,* &c., are oxydised more easily by fuming than by dilute nitric acid. Their combinations with the metals are likewise dissolved by nitric acid, but generally the metal is dissolved much sooner than the substance with which it is combined (see page 455, where I have indicated the sulphurets which are insoluble in nitric acid).

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[1] Or a specific gravity about 1·10.

* The substances which are INSOLUBLE in nitric acid are a few metals and oxydes before mentioned, the chloride, bromide, iodide, and cyanide of silver, and the bromate and iodate of oxyde of silver, the sulphate and seleniate of baryta, of strontia, of lime, and of oxyde of lead. The silicates behave towards nitric as towards muriatic acid.

* FUMING NITRIC ACID is used for the purpose of oxydising the metallic sulphurets; but generally a more dilute acid is used, for example, of a specific gravity of 1·11 or 1·12.

* The substance which most generally contaminates nitric acid is MURIATIC ACID, the presence of which may be ascertained by means of *nitrate of silver,* which will produce a precipitate or a turbidness of chloride of silver. The presence of SULPHURIC ACID is detected by diluting the nitric acid under examination with water, and pouring a solution of *nitrate of baryta,* or of *chloride of barium,* which will then produce a precipitate of sulphate of baryta[1], if sulphuric acid be present. The fixed substances may be detected by evaporating a small portion of the acid in a watch-glass.

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[1] The acid under examination and the test must both be dilute, otherwise a precipitate of nitrate of baryta might be formed, and thus mistaken for sulphate of baryta. In case, however, of a precipitate being produced, water must be somewhat largely added, which will leave the precipitate undissolved, if it be one of sulphate of baryta. This observation applies also when *nitrate of silver* is employed.—ED.

3. AQUA REGIA.

(Chloronitric Acid.)

This acid dissolves not only all the substances which are soluble in nitric acid, but also gold, platinum, and several other metals which are insoluble in the latter acid. It dissolves also, especially when there is an excess of muriatic acid, oxydes of antimony, peroxyde of tin, &c., and their salts. The other oxydised compounds which are insoluble in muriatic acid and in nitric acid, are likewise insoluble in *aqua regia*.

3. SULPHURIC ACID.

(Acide Sulfurique.)

* Concentrated sulphuric acid is used for the purpose of detecting *boracic acid* (page 281) and the *volatile acids; chloric acid* (page 246), *bromic acid* (page 255), in their salts; *bromine* (page 429), *iodine* (page 436), and *fluorine* (page 438), in their combinations with the metals. The acid, diluted with six or eight times its bulk of water, serves to detect and to precipitate *baryta* (page 24), *strontia* (page 29), *oxyde of lead* (page 98), and *lime* (page 34). Instead of dilute sulphuric acid, a solution of *sulphate of potash* may, in some cases, be advantageously substituted, as we have shown (page 34).

* Almost all the substances which resist the action of other acids are dissolved with the help of heat by concentrated sulphuric acid; yet it is but very seldom used for dissolving the substances which are insoluble in water, because the excess of this acid cannot be volatilised except by a high temperature, and also because the volatilisation of the sulphate of ammonia resulting from the supersaturation of the acid solution with ammonia is often inconvenient.

* The substances which are insoluble in sulphuric acid are gold and platinum, a few metals, and certain oxydised compounds, which are also insoluble in nitric and in muriatic acids. A few of the latter substances, however, are soluble in hot concentrated sulphuric acid, but are precipitated from such a solution by the addition of water.

* The sulphuric acid ordinarily used for analytical researches is distilled sulphuric acid. It is pure only when a few drops evaporated in a small platinum crucible leave no residuum. The sulphuric acid of commerce, however, is contaminated by small quantities of SULPHATE OF LEAD, owing to which, a solution of sulphuretted hydrogen gives it a brownish tinge[1]. Sometimes, also, it contains SULPHATE OF POTASH, which after evaporation remains in the platinum crucible. Or it may contain SELENIC ACID, by which it acquires the property of attacking gold, and even, if contaminated with MURIATIC ACID, that of attacking platinum. The presence of *selenic acid* is ascertained by diluting the acid under examination with a little water, and boiling it with muriatic acid, after which it may be left to digest with a sulphite (page 220). If the sulphuric acid contain any *arsenious acid*, it may be detected by passing a stream of sulphuretted hydrogen through the suspected acid previously diluted with water (page 341)[2]. If the acid contain NITRIC ACID, it may be detected by pouring in the undiluted acid a solution of protosulphate of iron (page 233), or, after diluting it with a little water, by *copper filings* (page 235).

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[1] The brownish tinge may also be the result of the presence of protoxyde of tin. When the concentrated acid contains sulphate of lead it becomes turbid when diluted with five or six times its bulk of water, because sulphate of lead, though soluble in concentrated sulphuric acid, is insoluble in the dilute acid. Sulphate of lead may be removed by allowing it to subside, after which the acid is fit for analytical purposes, if it contain no other impurity.—ED.

[2] The precipitate which may then fall down might be produced by the presence of arsenious acid, or of protoxyde of tin ; but the former is yellow, while the second is dark brown ; but if peroxyde of tin be present the precipitate is yellow also : the means of distinguishing these different impurities will be shown hereafter. A ready method, however, of detecting whether the acid contains arsenic, consists in diluting it with water, and putting some pure zinc into it ; the hydrogen which will then disengage being passed through a red-hot glass tube, must not deposit the least trace of arsenic. See the Article on Arsenic and Arsenious Acid, page 331, also page 338.

It is clear that when sulphuric acid contains arsenic, it must be either rejected or purified, before it can be used in Marsh's apparatus. The acid may, however, be purified by diluting it with about six times its bulk of water, supersaturating the liquid with sulphuretted hydrogen, and leaving the mixture for some time in a moderately warm place until perfectly clear. The sulphuret of arsenic produced may then be separated by filtering, and the filtered acid is to be boiled until all odour of sulphuretted hydrogen has vanished. Before putting by the acid for subsequent use, it should again be tested, to make certain that it is pure.—ED.

5. AMMONIA.

(*Ammoniaque.*)

* AMMONIA is particularly used for saturating acid liquids, for which purpose it is preferable to the solution of the fixed alkalies. It is likewise used for distinguishing the solutions of the salts of alkalies, of baryta, of strontia, of lime, from those of magnesia, alumina, and other earths; the latter being precipitated by ammonia, whilst the former are not. It is also resorted to for the purpose of detecting protoxyde of copper (page 118) and oxyde of nickel (page 80); of dissolving chloride of silver, (page 128), and distinguishing it from subchloride of mercury, and from chloride of lead; in a word, to precipitate a multitude of oxydes. Like muriatic acid, ammonia is a re-agent which cannot be dispensed with.

* Ammonia must be as clear as water; the slightest tinge of brown indicates the presence of *organic substances*. Evaporated in a platinum spoon or crucible, it must not leave the slightest residuum, and when saturated with pure muriatic acid, the mixture must, on evaporation, yield a salt which is completely volatilisable without leaving any carbonaceous residuum before its complete volatilisation. Ordinarily, however, the purest ammonia being submitted to this test, leaves an exceedingly small residuum of charcoal, which, if it be at all considerable, renders the ammonia unfit for analytical research.

* Ammonia is often contaminated by MURIATE OF AMMONIA, SULPHATE OF AMMONIA, CARBONATE OF AMMONIA, CARBONATE OF LIME or of BARYTA, CHLORIDE OF CALCIUM; sometimes also it contains traces of PEROXYDE OF TIN, PROTOXYDE OF COPPER. If then it be supersaturated by pure *nitric acid*, and tested by solution of *nitrate of silver*, a white precipitate of chloride of silver will indicate the presence of MURIATE OF AMMONIA. If, after supersaturating the solution of ammonia by either nitric or by muriatic acid, the further addition of *chloride of barium* and of a sufficient quantity of water produces a white precipitate, it is a proof that the alkali contains SULPHATE OF AMMONIA. If

the ammonia contains CARBONIC ACID, which is often the case when it has not been kept carefully sheltered from the contact of the air, the addition of *lime water*, or of a solution either of *chloride of calcium* or of *chloride of barium*, will render it turbid, owing to the formation of carbonate of lime, or of baryta[1]. Ammonia may sometimes contain *chloride of calcium*, in which case it will leave a residuum by evaporation, and be rendered turbid by solution of *oxalic acid*. If it contain traces of oxyde of tin, a residuum will be left after the evaporation of a large quantity of the liquor, which residuum being mixed with soda, and reduced at the interior flame of the blow-pipe, will yield metallic tin (page 175). Ammonia may sometimes contain OXYDE OF COPPER, in which case, if the quantity be not too minute, the ammonia will have a bluish tinge, but the presence of this oxyde may be rendered more apparent by adding *hydrosulphuret of ammonia*, which will precipitate sulphuret of copper, in which the presence of even a most minute trace of copper may be detected by means of the blow-pipe.

6. PURE HYDRATE OF POTASH.

(*Hydrate Potassique pur.*)

* IN the state of solution, pure HYDRATE OF POTASH serves for the detection of ammonia in ammoniacal compounds (page 21). It is also used for separating and distinguishing the solutions of alumina (page 44), of oxyde of tin (page 173), of oxyde of lead (page 96), and of a few other earths and metallic oxydes, from that of other bases which are likewise precipitated by potash, but which are not re-dissolved by an excess of this re-agent. Solution of hydrate of potash dissolves also a considerable number of oxydes, especially those which behave like acids towards the bases.

* *Hydrate of potash* in the solid state seems to absorb certain gases, such as, for example, *carbonic acid*, *chlorine*, *sulphuretted hydrogen*, &c. Formerly it was frequently employed for fusion

with certain oxydes, especially those which behave like acids, and which, after ignition, have become insoluble in muriatic acid: they were thus converted into compounds soluble in acids. Now, *carbonate of potash* or *of soda* is preferred in most cases to *hydrate of potash*.

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[1] Of course, if chloride of barium be used, the absence of sulphuric acid must first be ascertained.—ED.

* Solution of potash may contain CHLORIDE OF POTASSIUM, SULPHATE OF POTASH, and sometimes also NITRATE OF POTASH. If, when supersaturated with *pure nitric acid*, a solution of *nitrate of silver* determines a white turbidness of *chloride of silver*, CHLORIDE OF POTASSIUM is present. It is very rare, however, to find potash altogether free from chloride of potassium. If, after dilution, the addition of *chloride of barium* renders it turbid, SULPHATE OF POTASH is present. NITRATE OF POTASH is detected by the methods already indicated (page 234, &c.). Frequently the solution of potash contains *silicic acid* and *alumina*, which substances may be discovered by supersaturating with muriatic acid, evaporating to dryness, moistening the residuum with muriatic acid, and, after a while, pouring water upon it; if *silicic acid* was present, it then remains insoluble; if, on the contrary, the dried mass, being moistened with muriatic acid, dissolves completely, the conclusion is, that it contained no silicic acid. By adding to the acid filtered liquor an excess of solution of *carbonate of ammonia*, the ALUMINA, if any, is then precipitated.

* The solution of *hydrate of potash* generally contains a little carbonate of potash, the presence of which is, in most cases, of no consequence, provided not too abundant, which may be recognized by the strong effervescence which is produced by saturating it with an acid.

* If the solution of *potash* contains traces of LIME, a white precipitate of oxalate of lime is produced when, after adding a little water and a solution of oxalic acid to the liquor, the whole is boiled.

* When *solid potash* is employed for the purpose of absorbing gases, it is not necessary that it should be quite pure.

7. CARBONATE OF POTASH.

(*Carbonate Potassique.*)

* Solution of *carbonate of potash* may be replaced by one of *carbonate of soda,* which in most cases acts in the same manner. The solutions of these alkaline carbonates precipitate a great number of metallic oxydes, and all the earths, from the solutions of their salts, by which means many of the latter are distinguished from the alkalies on which the solution of the alkaline carbonates has no action. In the dry way, *carbonate of potash* or *of soda* is employed to decompose the compounds of silicic acid (page 286), and in general the substances which resist the action of the acids. They are also used for separating certain acids from certain earths and metallic oxydes, especially when the combinations are insoluble in water; the substance is fused with an excess of alkaline carbonate, and the fused mass is treated by water, which dissolves the acid united with the alkali, and also the excess of the alkaline carbonate, the earth and the metallic oxyde being left undissolved when not soluble in solution of alkaline carbonate.

* Carbonate of potash or of soda very often contains some SULPHATE OF ALKALI, and some CHLORIDE OF POTASSIUM, or of SODIUM, which may be distinguished by the same means which are employed for testing the purity of potash. Carbonate of potash frequently contains silicic acid, and occasionally also traces of alumina, which may be detected in the same manner as for testing the purity of hydrate of potash. It is very difficult to procure *carbonate of potash* perfectly free from silicic acid; as *carbonate of soda* does not contain any, it is employed in preference. Sometimes, however, *carbonate of soda* contains small quantities of SULPHURET, of SULPHITE, or even of HYPOSULPHITE OF SODA. The presence of a free alkaline SULPHURET is recognizable by the odour of sulphuretted hydrogen, which is disengaged by supersaturating a large quantity of the salt by an acid; if, on the contrary, the odour is that of

sulphurous acid, it may be owing to the presence of a SULPHITE or of a HYPOSULPHITE OF SODA; the presence of the latter substance is accompanied by a separation of sulphur. Very minute traces of HYPOSULPHITE OF SODA may be detected by adding a little *nitrate of silver* to the solution, and then dilute *nitric acid* to re-dissolve the precipitate; the liquor assumes then a brownish tinge, due to a production of sulphuret of silver (page 216), which, after a short time, is precipitated in the form of a brownish-black deposit.

8. CARBONATE OF AMMONIA.

(*Carbonate Ammoniacal.*)

* THE solution of *carbonate of ammonia* may, in most cases, be employed like that of carbonate of soda or of potash. There are, however, many instances in which carbonate of ammonia must be preferred, as, for example, for the purpose of separating the earths from the alkalies, and for dissolving glucina and other bases.

* Like ammonia, *carbonate of ammonia* often contains MURIATE OF AMMONIA, SULPHITE OF AMMONIA, and ORGANIC SUBSTANCES; all of which substances may be detected in the same manner as in ammonia. Pure carbonate of ammonia should evaporate without residuum when heated in a platinum crucible or spoon. If it contain any CARBONATE OF LEAD, a residuum of oxyde of lead will then be left; the same would be the case with a SALT OF LIME. When a plombiferous ammoniacal carbonate is treated by water, the *carbonate of lead* remains undissolved.

9. SULPHURETTED HYDROGEN.

(*Sulfide Hydrique.*)

* THE aqueous solution of *sulphuretted hydrogen gas* is generally used in chemical analysis. Yet sometimes it is better to pass the current of the gas itself through the liquor under examination. *Sulphuretted hydrogen* is a most important and infallible re-agent for detecting the metallic oxydes. Considering that some metallic oxydes are precipitated by it from their ACID solutions, whilst other metallic oxydes are precipitated by

it only from their ALKALINE solutions, whilst the ALKALIES and EARTHS are not precipitated by it at all, it is advisable to ground the systematic course of analysis upon the behaviour of the different substances towards *sulphuretted hydrogen* or towards *hydrosulphuret of ammonia.* We have treated of this re-agent most minutely in the first part of this volume, and again presented a summary table of its reactions at page 471. The solution of sulphuretted hydrogen employed in qualitative analysis must be as saturated as possible; it is necessary to preserve it in well-corked flasks of moderate size, because by exposure to the air it is often decomposed, and becomes unfit for use[1] (page 448). As this re-agent is always prepared by the operator, it cannot contain any foreign matter.

* When, in preparing the solution of sulphuretted hydrogen, the current of the gas disengaged from the mixture of sulphuret of iron, and dilute sulphuric acid is too rapid, the gas may carry off with it small portions of sulphuric acid and of proto-sulphate of iron, and the liquor, which then produces a black precipitate of sulphuret of iron when ammonia is added to it, may be a source of numerous errors in qualitative analysis[2].

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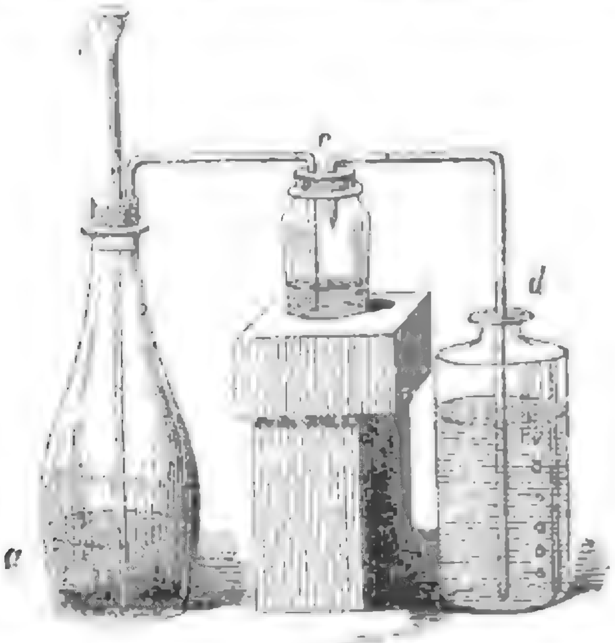
[1] The best way of keeping aqueous solution of sulphuretted hydrogen for a long time is, immediately after having prepared a convenient quantity of it, to pour it into a number of small phials, containing about a quarter of a pint, to cork them soundly, and to invert them into tumblers or vessels full of water.—ED.

[2] The following apparatus should therefore be always employed :—



a is a bottle containing the mixture of sulphuret of iron and sulphuric acid ; *b* is the

10. HYDROSULPHURET OF AMMONIA.

(*Sulfhydrate Ammonique.*)

* *Hydrosulphuret of ammonia* is used instead of sulphuretted hydrogen for precipitating the metallic oxydes from neutral or from alkaline solutions.

* The ammonia must be saturated by sulphuretted hydrogen gas as much as possible[1]. The gas must be passed through a solution of ammonia. The solution of ammonia should be previously diluted with three or four times its bulk of water. When this re-agent is kept in badly-corked flasks, or when the flasks which contain it are too frequently opened, it turns yellow, and if left for a long time exposed to the air, it becomes partially converted into hyposulphite of ammonia, and can no longer be used as a re-agent. If, when an excess of muriatic acid is poured in hydrosulphuret of ammonia, a very abundant white precipitate of sulphur is formed, the re-agent is no longer fit for use; but if this precipitate is not very abundant, and if its formation is at the same time accompanied by a copious disengagement of sulphuretted hydrogen, the re-agent may still be employed. If, during the preparation, the current of sulphuretted hydrogen disengaged from a mixture of sulphuret of iron and of dilute sulphuric acid has been too rapid, the hydrosulphuret of ammonia obtained will, after some time, deposit black flakes of sulphuret of iron[2]. If this re-agent be kept in bottles, the

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funnel for pouring the acid; *c* is a small bottle half full of water, for washing the sulphuretted hydrogen gas disengaged; *d* is a larger bottle, three-quarters filled with distilled water, which has been previously boiled to free it from air, and which must be as cold as possible. The disengagement must be continued until the water is saturated, which may at once be known, says Dr. Fresenius, by closing the mouth of the bottle *d* with the thumb, and strongly shaking the contents. If the thumb be gently pushed off, the water is saturated; if, on the contrary, it be sucked in, the disengagement must be continued. When a liquid has to be tested by a current of sulphuretted hydrogen gas, the same apparatus should be employed, substituting a beaker containing the liquid under examination for the bottle *d*.—Ed.

[1] This is known to be the case when the addition of solution of sulphate of magnesia ceases to produce a precipitate in the mixture.—Ed.

[2] This may be prevented by using the apparatus mentioned in note 2, page 549.—Ed.

glass of which contains much oxyde of lead, a black precipitate of sulphuret of lead will in course of time be formed[1].

11. CHLORIDE OF BARIUM.

(*Chlorure Barytique.*)

* The solution of *chloride of barium* is used not only to detect sulphuric acid and the solutions of sulphates (page 202), but likewise to precipitate a very great number of acids, which form with baryta, salts which are insoluble in water. There are but few cases in which, instead of the solution of *chloride of barium*, NITRATE OF ACETATE OF BARYTA are employed. *Acetate of baryta* is more especially resorted to for separating magnesia from the alkalies.

* *Chloride of barium* and *nitrate of baryta* are seldom impure; they may, however, contain very small portions of CHLORIDE OF STRONTIUM and of NITRATE OF STRONTIA, which may be detected by digesting these salts in alcohol, which would then burn with a red flame. If the chloride of barium be yellow, it may be owing to the presence of PERCHLORIDE OF IRON. If it powerfully attracts moisture from the air, it contains CHLORIDE OF CALCIUM.

Both the *barytic chloride* and *nitrate* should, however, dissolve completely in water, and yield a limpid solution. It must not be rendered turbid by addition of ammonia[2], and after being mixed with an excess of sulphuric acid, and separating the precipitate by filtering, the filtered liquid must not leave the slightest fixed residuum after evaporation to dryness; should one be left, it would be a proof that the barytic salt contained a salt of alkali.

* ACETATE OF BARYTA yields sometimes with water a solution which is not perfectly clear. It contains sometimes MURIATIC

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[1] Sulphuret of potassium is used for separating copper in the state of sulphuret of copper, instead of *hydrosulphuret of ammonia*, in which latter re-agent it is slightly soluble. Solution of *sulphuret of potassium* must always be prepared fresh for the occasion.—Ed.

[2] Nor by hydrosulphuret of ammonia, nor by sulphuretted hydrogen; and it must be perfectly neutral to test paper. These tests are the same for *nitrate of baryta*; but in the latter case the addition of nitrate of silver to its solution must not produce any white precipitate or turbidness of chloride of silver, which would indicate the presence of muriatic acid.—Ed.

ACID, which then renders it unfit to be used as a [special] re-agent, particularly for separating the alkalies from magnesia. The presence of muriatic acid is detected by dissolving the acetate in a very large quantity of water, and adding to the liquor a little pure nitric acid and nitrate of silver, which will produce a precipitate of chloride of silver.

12. NITRATE OF SILVER.

(Nitrate Argentique.)

* SOLUTION of *nitrate of silver* serves principally to detect *muriatic acid* and the solutions of *metallic chlorides* (page 420). It is used also for the detection of many acids which form with oxyde of silver compounds which are insoluble or sparingly soluble in water, such as *bromic acid* (page 255), *iodic acid* (page 259), *phosphoric acid* (page 262), *boracic acid* (page 280), *arsenic acid* (page 333), *arsenious acid* (page 341), *hydrobromic acid* (page 426), and the solutions of *metallic bromides* (page 426), *hydriodic acid* (page 431), and the solutions of *metallic iodides* (page 431).

* In a few rare cases, however, SULPHATE and ACETATE OF SILVER are employed instead of the NITRATE[1].

* The solution of nitrate of silver must not turn bluish by addition of ammonia, which would indicate the presence of OXYDE OF COPPER. If the silver be precipitated from the solution in the state of chloride of silver by means of muriatic acid, the liquor filtered from this precipitate being evaporated in a *porcelain* [or watch-glass] *capsula* must leave no fixed residuum[2], which is the case when the fused nitrate of silver has been adulterated with nitrate of alkali[3].

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[1] We may further mention here amongst these re-agents the AMMONIO-NITRATE OF SILVER, which is used for the detection of arsenic.—ED.

[2] The filtered liquid here mentioned should not be precipitated or coloured by sulphuretted hydrogen.—ED.

[3] The presence of nitrate of potash may also be detected by heating a small portion of the suspected nitrate of silver before the blow-pipe upon charcoal, which will cause a deflagration, and the portion on which it has taken place reacts then like an alkali. Sometimes also nitrate of silver is adulterated by nitrate of lead, which may be easily detected by adding sulphuric acid, which will precipitate the lead in the state of sulphate.—ED.

13. MURIATE OF AMMONIA.

(*Chlorure Ammonique.*)

* THE solution of *muriate of ammonia* is employed to prevent the precipitation of some bases, such as *magnesia, protoxyde of manganese, oxyde of zinc, oxyde of nickel, oxyde of cobalt,* &c., by ammonia or by the solutions of the fixed alkaline carbonates, so as to be able to separate these substances from other bases. It is also sometimes used in qualitative analysis to precipitate *alumina* from its solution in potash (page 44), and likewise to precipitate *platinum, iridium,* &c.

* If *muriate of ammonia* be not at hand, the same result may be obtained by acidifying the solution under examination with *muriatic acid* and then adding *ammonia*[1].

* In most cases other salts of ammonia may be substituted, but muriate of ammonia is the least expensive.

* MURIATE OF AMMONIA sometimes contains *sulphate of ammonia,* which may be detected in the solution of the salt by means of a solution of chloride of barium. Yet, in most cases, the presence of sulphate of ammonia is of no consequence in qualitative analysis. The sal ammoniac may also contain *chloride of sodium,* or *sulphate of soda,* or *of magnesia.* These impurities are detected by heating a small quantity of the salt upon a platinum spoon or crucible, which will then leave a residuum. If before the complete volatilisation of the salt an abundant residuum of charcoal be observed, it is a proof of the presence of *organic matter.* That of *bromide of ammonia* is detected by means of the aqueous solution of chlorine and ether (page 427). The presence of *metals* is easily detected by sulphuretted hydrogen, and hydrosulphuret of ammonia[2].

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[1] Not only is the same result thus obtained as by using a solution of muriate of ammonia, but if there be much free acid in the solution of the substance under examination, the addition of ammonia will create a sufficient quantity of muriate or of other ammoniacal salt, and render the addition of the solution of the muriate or other salt of ammonia superfluous.—ED.

[2] The solution of muriate of ammonia should be perfectly neutral to test papers, and not precipitated or acted upon by hydrosulphuret of ammonia.—ED.

14. OXALIC ACID.

(*Acide Oxalique.*)

* INSTEAD of the solution of this acid, that of BINOXALATE OF POTASH of commerce (sorrel salt) may generally be used. The employment of the pure acid is required only in a small number of circumstances. It is useless in qualitative analysis to have OXALATE OF AMMONIA prepared beforehand, because it may always be very easily produced by adding a slight excess of ammonia to the solution of oxalic acid. The solutions of the oxalates serve principally, in certain cases, to detect lime in the salts which are soluble in water (page 35), but they are also employed to precipitate several metallic oxydes.

* The BINOXALATE OF POTASH of commerce may be adulterated by *tartrate of potash,* or may contain organic impurities. The easiest method of testing consists in boiling a portion of it with concentrated sulphuric acid, by which it is decomposed and dissolved under disengagement of gases (page 389). If the solution thus obtained remains colourless, the salt is pure; but if it turn brown or black by a prolonged ebullition, and if a distinct odour of sulphurous acid is evolved, it indicates the presence of tartaric acid or of other organic substances. *Binoxalate of potash* is known to be mixed with *bisulphate of potash* when the solution, being treated by chloride of barium and a little free muriatic acid, yields a precipitate of sulphate of baryta. *Binoxalate of potash* being decomposed by heat must leave a residuum of carbonate of potash, which is neither pure white nor black, but of a greyish colour.

* The presence of *organic substances* in OXALIC ACID may be detected by *sulphuric acid* in the same manner as in binoxalate of potash. If it contain *sulphuric acid* it may be detected by diluting its solution, and adding thereto a dilute solution of chloride of barium, which in that case will produce a precipitate of sulphate of baryta, which, however, requires some time for its precipitation, when only feeble traces of sulphuric acid are

present. *Oxalic acid,* when heated in a platinum crucible or spoon, must volatilise completely, during which it is partly decomposed: it must not turn black before complete evaporation, nor leave any fixed residuum. Pure oxalic acid does not become moist by exposure[1].

15. PHOSPHATE OF SODA.

(Phosphate Sodique.)

* Solution of phosphate of soda is principally used for the detection of magnesia (page 40), and for distinguishing it in acid solutions from the alkalies; it serves likewise to precipitate the earths and many metallic oxydes.

* *Phosphate of soda* is often contaminated by *sulphate of soda,* the presence of which is very easily ascertained by adding some muriatic or nitric acid to the dilute solution of the salt, and then a solution of a baryta salt, which produces a white precipitate of sulphate of baryta. The presence of *chloride of sodium* is shown by the precipitate of chloride of silver, which a solution of nitrate of silver determines, after acidifying the solution under examination with nitric acid. If *phosphate of soda* is contaminated by *carbonate of soda,* the presence of the latter is rendered manifest by moistening the salt with a little water, and pouring an acid thereon, which will cause a disengagement of carbonic acid gas. When a solution of *carbonate of soda* renders one of *phosphate of soda* turbid, especially with the help of heat, it is a proof that the latter is contaminated by an earthy base. Sometimes *phosphate of soda* may contain some *arsenic* or *arsenious acids,* in which case its solution, after addition of muriatic acid, yields, by treatment with sulphuretted hydrogen, a sulphuret of arsenic in which metallic arsenic must be sought for (page 347).

* Pure *phosphate of soda* fuses at a red heat into a limpid bead, which becomes like an enamel on cooling.

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[1] Oxalic acid frequently contains nitric acid. This impurity is detected because the solution, when boiled with a small quantity of sulphate of indigo, is then decolorised.—Ed.

* *Phosphate of soda*, after exposure to a low red heat, yields a solution which in some respects behaves in a manner different from that of the uncalcined salt, especially towards solution of nitrate of silver (page 262). It is advisable, therefore, to test this salt with solution of silver, in order to acquire the proof, by the formation of the yellow precipitate, that it has not been calcined[1].

16. CHLORIDE OF PLATINUM.

[BI OR PERCHLORIDE OF PLATINUM.]

(*Chlorure Platinique.*)

* THE concentrated aqueous solution of platinum[2] is used only as a test for potash (page 4) and ammonia (page 20).

* This re-agent is usually prepared by the operator by dissolving platinum foil, or spongy platinum, or pieces of platinum crucibles, or other utensils out of service, in aqua regia. The solution is to be evaporated almost to dryness, in order to expel most of the free acid; the mass is then dissolved in a small quantity of water, and filtered.

* Although it is advantageous in many cases to employ an alcoholic solution of chloride of platinum, yet it is better to preserve it in the state of concentrated aqueous solution, because the other becomes decomposed in course of time, and when it is wanted, alcohol may be used instead of water to dissolve the combination under examination, or to dilute the solution, especially if the compound be soluble in alcohol.

17. HYDROFLUOSILICIC ACID.

(*Acide Siliciflúorhydrique.*)

* HYDROFLUOSILICIC ACID is used as a test for distinguishing *baryta* from *lime* and from *strontia* (pages 24—35—30). In this

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[1] If ammonia be added to a solution of phosphate of soda, and heat be applied, it must not become turbid; and the precipitates produced by the solution of chloride of barium and of nitrate of silver must be completely soluble in dilute nitric acid, otherwise a sulphate or a chloride is present.—ED.

[2] This solution consists generally of one part of chloride in eight or ten parts of water.—ED.

respect it is a re-agent that cannot be dispensed with, as no other can replace it. Sometimes it is resorted to as a test for potash (page 4).

* This re-agent is ordinarily prepared by the operator by causing a current of fluosilicic gas to pass through water, but in order to prevent the glass tube from being stopped by the silicic acid [hydrated silicic acid], which separates, the tube must plunge into a small quantity of mercury placed at the bottom of the water. The silicic acid may afterwards be separated by filtering, and the filtered liquid is employed as re-agent.

18. FERROCYANIDE OF POTASSIUM.

(*Cyanure Ferrosopotassique.*)

* SOLUTION OF FERROCYANIDE OF POTASSIUM is used for detecting many metallic oxydes, but more especially *peroxyde of iron* (page 90) and of *copper* (pages 117—120). Yet, for reasons which have been given before (page 488), it is not to be depended upon except under certain conditions.

* The *ferrocyanide of potassium* of commerce contains sometimes *sulphate of potash*, the presence of which may be detected in the dilute solution of the salt by the precipitate of sulphate of baryta which an addition of a barytic salt determines then in it. The crystals of this salt must be of a lemon-yellow colour, soluble in alcohol.

19. FERRICYANIDE OF POTASSIUM.

(*Cyanure Ferricopotassique.*)

* THE solution of *ferricyanide of potassium* is used especially as a test for *protoxyde of iron* in a solution which contains *peroxyde of iron* at the same time (page 93). It may also be employed as a test for many other metallic oxydes, yet, for reasons which have been developed before (page 489), it is to be trusted only under certain conditions[1].

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[1] The reasons are summarily, that both the ferro and the ferricyanide of potassium are partially decomposed when mixed with solutions of strong acids, in consequence of which Prussian blue is formed at the expense of the re-agent itself, hydrocyanic acid being at the same time disengaged.—ED.

20. CHLORIDE OF CALCIUM.

(*Chlorure Calcique.*)

* THE solution of chloride of calcium is rarely used, for example, for precipitating *phosphoric acid,* but it may very well be replaced by a solution of chloride of barium.

* The solution of *chloride of calcium* is pure, if it yield no precipitate with ammonia, for if one be produced, it is a proof of the presence of *phosphate of lime,* or other analogous substances. When the solution, being mixed with ammonia, becomes slightly turbid, and if the addition of hydrosulphuret of ammonia renders it blackish, it is a sign of the presence of perchloride of iron, or other metallic compounds[1].

21. ACETATE OF LEAD.

(*Acétate Plombique.*)

[NEUTRAL ACETATE OF LEAD.]

THE solution of neutral ACETATE OF LEAD is sometimes used as a test for *phosphoric acid* (page 262).

* There are a few cases in which NITRATE OF LEAD is used in preference.

* The *acetate of lead* of commerce sometimes contains *acetate of lime,* which is detected as follows:—To the solution of the acetate of lead add a solution of sulphuretted hydrogen until the whole of the oxyde of lead has precipitated in the state of sulphuret of lead; the *lime,* if present, may then be detected in the liquid filtered from the sulphuret by supersaturating it with ammonia, and adding a solution of oxalic acid, or of binoxalate of potash, which determines a precipitate of oxalate of lime. If after saturating the filtered liquid with ammonia, hydrosulphuret of ammonia be then added, and a black precipitate be then formed, it is a sulphuret of iron which indicates that the salt

under examination was contaminated by *iron*. If the solution of the salt becomes bluish when saturated by ammonia, it is a sign of the presence of *copper*.

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[1] The solution of chloride of calcium should not evolve any ammonia when mixed with hydrate of potash or of lime, and it should be perfectly neutral to test papers. —ED.

* The employment of the BASIC ACETATE OF LEAD is rare[1].

22. PROTOSULPHATE OF IRON.

(*Sulfate Ferreux.*)

* RECENTLY dissolved in water, it is used as a test for *gold* (page 170), *nitric acid* (page 233), and *nitrous acid* (page 240).

* When the solution contains a little peroxyde of iron, which is always the case if care has not been taken to shelter it altogether from the contact of the air, it may be detected by means of hydrocyanic acid (page 484).

* The *protosulphate of iron* of commerce (green copperas) frequently contains *protosulphate of copper* (blue copperas), *sulphate of zinc* (white copperas), *sulphate of magnesia*, and other sulphates, the presence of which, however, is not objectionable in most qualitative analyses; but no trace of these impurities can of course exist in a salt prepared by the operator himself, by dissolving iron in dilute sulphuric acid; the sulphate of iron which results from the re-action of dilute sulphuric acid upon sulphuret of iron in the preparation of sulphuretted hydrogen, is also very pure.

23. PROTOCHLORIDE OF TIN.

(*Chlorure Stanneux.*)

* THE recently-prepared solution of PROTOCHLORIDE OF TIN, to which enough muriatic acid is added to render it clear, is used as a test for *oxyde of gold* (page 171), and also to reduce certain metallic oxydes of easy reduction.

* The *protochloride of tin* of commerce contains often a small quantity of peroxyde of tin, which does not completely dissolve when the salt is prepared with very dilute muriatic acid, in

which case it is to be separated by filtering. A small quantity of this oxyde is not objectionable in qualitative analysis [1].

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[1] This re-agent is more especially used for detecting *sulphuretted hydrogen*, for which it is a more sensitive test than the neutral acetate.—ED.

* Treated by a small quantity of water and a large excess of hydrosulphuret of ammonia, protochloride of tin must dissolve completely (page 179); if a black metallic sulphuret remains undissolved, it may be *sulphuret of lead, of iron*, &c.

* The solutions of protosulphate of iron and of protochloride of tin are very liable to become unfit for use on account of their absorbing oxygen, wherefore they should only be prepared shortly before they are wanted.

24. ALCOHOL.

(Alcool.)

* ALCOHOL is used for precipitating *sulphate of lime* completely (page 37), to detect *boracic acid* (page 280), and for several other purposes.

* It is necessary that alcohol should be perfectly free from all foreign substance, and it must evaporate without any residuum [2].

25. DISTILLED WATER.

(Eau distillée.)

* DISTILLED water is the most important of all solvents, and as it is always used in analytical research, it is necessary that it should be absolutely pure. A few hundred grains of it being evaporated in a platinum crucible, must not leave any residuum whatever. It must not redden litmus paper, nor be rendered turbid by nitrate of silver [which would indicate the presence of a chloride]. Sometimes it contains traces of *sulphate of lime*, in which case it generally becomes turbid after a while by addition of chloride of barium, or a solution of oxalic acid and ammonia [3].

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[1] Sulphuric acid should not precipitate solution of protochloride of tin, nor render it turbid.—ED.

[2] The impurity of alcohol is generally a volatile oil, which passes with the distilled alcohol, and is called oil of grain or fusel oil [hydrated protoxyde of amyle]. Alcohol should not redden blue litmus paper.—ED.

[3] Distilled water should not be rendered turbid by lime water.—ED.

26. TEST PAPERS.

* LITMUS, TURMERIC, and BRAZIL-WOOD papers[1].

SPECIAL RE-AGENTS.

* THE re-agents enumerated above will suffice in most cases of qualitative analysis. Those which follow are used principally to examine more closely one or the other of the constituent principles isolated by analysis from the compound under examination, or for the purpose of analysing substances more rarely met with.

1. CHLORINE.

* THE aqueous solution of chlorine serves to detect *bromine* in the solution of *metallic bromides,* and *hydrobromic acid* (page 427). Sometimes it is resorted to as a test for *iodine* (page 433), and for the purpose of oxydising certain substances. *Aqueous solution of chlorine* is prepared by agitating together a mixture of gaseous chlorine and water, and the solution must be kept in small flasks[2]. This solution must decolorise litmus paper and solution of sulphate of indigo. If a large quantity of the re-agent is required to produce the last of these effects, it is a

proof either that it does not contain enough chlorine, or that it has gradually decomposed.

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[1] Blue litmus paper is used as a test for acids, and reddened litmus paper as a test for alkalies, by which it is rendered blue again: but it should be recollected that many or rather nearly all the neutral metallic salts re-act upon blue litmus paper as an acid, and consequently turn it red; whilst, on the other hand, the alkaline earths and the sulphurets, as well as the carbonates of alkalies, re-act in the manner of alkalies, and restore the blue colour of reddened litmus paper. The soluble salts of boracic acid and other weak acids possess also this property. Turmeric paper is used as a test for alkalies, by which it is turned brown. Turmeric paper is much less sensitive than all other papers, and may further be re-acted upon as by an alkali, as we have just said; by the sulphurets and carbonates of alkalies, by boracic acid and other substances. Brazil wood paper is bleached by several acids, such as sulphurous acid and other substances.—ED.

[2] This aqueous solution of chlorine, besides being kept in well stoppered small flasks, must further be carefully sheltered from the influence of solar or day light, otherwise it will be converted into a dilute solution of muriatic acid, because the water is decomposed, its hydrogen uniting with the chlorine (to form muriatic acid), whilst its oxygen is set free.—ED.

* In certain cases CHLORIDE OF LIME may be used instead of *aqueous solution of chlorine.*

2. ACETIC ACID.

(*Acide Acétique.*)

* ACETIC acid is sometimes used for the purpose of dissolving oxydised substances when it is unadvisable to resort to nitric or muriatic acid to produce that effect.

* It must be moderately strong, of a specific gravity of about 1·04. It must be free from *muriatic* and from *sulphuric acids*, and likewise from *metallic bodies*[1].

3. TARTARIC ACID.

(*Acide Tartrique.*)

* THE concentrated solution of TARTARIC ACID serves to detect *potash* (page 6), and also to distinguish it from *soda* (page 10), from lithia (page 16), and even from ammonia (page 20); it should not be preserved in too large quantity, because it easily turns mouldy[2].

* *Tartaric acid* must dissolve completely in alcohol; if it contain a *salt of lime,* alcohol will in most cases fail in dissolving it completely[3], and after ignition upon a platinum foil a residuum will be left after burning the carbon with the blow-pipe. The solution of *tartaric acid,* to which a salt of baryta is added, will yield a precipitate of sulphate of baryta, if it be contaminated

by sulphuric acid; the *metallic bodies* which might be found mixed with it may be detected either by sulphuretted hydrogen, or after saturating with ammonia, by hydrosulphuret of ammonia.

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[1] Neither should it contain *sulphurous acid* nor *nitric acid;* the latter may be detected by boiling with solution of sulphate of indigo; and if addition of nitrate of baryta added to the solution of acetic acid boiled with nitric acid produces a precipitate, it indicates the presence of sulphurous acid. Acetic acid, if pure, must evaporate without residuum.—ED.

[2] It is therefore better to keep tartaric acid in the dry state, and to dissolve a little of it when wanted. It is frequently used to prevent the precipitation of several metals by alkalies, by forming with them double tartrates, which are not decomposed by alkalies.—ED.

[3] The *salt of lime* may be detected in solution of tartaric acid by neutralising with ammonia and adding oxalate of ammonia, which will then yield a white precipitate of oxalate of lime.—ED.

4. SULPHATE OF ALUMINA.

(*Sulfate Aluminique.*)

* SOLUTION of SULPHATE OF ALUMINA is employed to detect potash (page 5), and ammonia (page 21); yet it is a re-agent which may be almost dispensed with. The best method of preparing it consists in taking the pure alumina which is obtained in the qualitative analysis of substances which contain no potash, and to pour sulphuric acid upon it, heating the whole until the excess of sulphuric acid has almost entirely evaporated. The mass may then be dissolved in a little water, and filtered. If the sulphate of alumina thus obtained be too strongly heated, it may lose part or even all its sulphuric acid, in which case it is insoluble in water.

5. NITROPICRIC ACID.

[CARBAZOTIC ACID.]

(*Acide Nitropicrique.*)

* THIS acid is used as a test for potash: it is the most sensitive test for the purpose (page 16).

6. SUCCINATE OF AMMONIA.

[NEUTRAL SUCCINATE OF AMMONIA.]

(*Succinate Ammonique.*)

* THE neutral solution of *succinate of ammonia* is sometimes used to distinguish *baryta* from *strontia*, and from *lime*, when hydrofluosilicic acid is not at hand (pages 26, 30, 36); but it is more especially used in qualitative analysis to separate small quantities of *protoxyde of manganese*, and of other oxydes mixed with *peroxyde of iron*.

* When the liquor filtered from the persuccinate of iron produced contains already salts of fixed alkalies, SUCCINATE OF SODA may be used instead of *succinate of ammonia*.

* [Neutral] *succinate of ammonia* cannot be kept otherwise than in solution, for the salt which crystallises from a neutral solution is an acid salt[1]. It is, however, advisable to prepare the neutral solution only in small quantities, because it soon turns mouldy. SUCCINATE OF SODA, on the contrary, in the crystalline state, is a neutral salt.

* As both *succinate of ammonia* and *succinate of soda* are prepared by the operator, they cannot but be pure, provided the succinic acid employed be itself pure. Pure *succinic acid* is perfectly soluble in alcohol, and is completely volatilised by a red heat when placed upon platinum foil. On the contrary, if it contains *tartaric acid*, a voluminous residuum of charcoal is left. Whether the acid be mixed with fixed bodies or not may be ascertained in the same manner, such as, for example, with *sulphate* or *binoxalate of potash*. Treated by potash, no odour of *ammonia* must be evolved, otherwise this would prove that it contains an ammoniacal salt, for example, *muriate of ammonia*. *Succinic acid* must be almost entirely free from empyreumatic oil, and have a white colour. Its solution mixed with one of a persalt of iron must not prevent the precipitation of the peroxyde of iron by addition of an excess of ammonia; for otherwise it would prove the presence of *tartaric acid*, or of other non-volatile organic substances.

* The BENZOATES OF ALKALIES were formerly used occasionally to separate *peroxyde of iron*, but their employ is less convenient than that of the succinates.

7. SULPHATE OF MAGNESIA.

(Sulfate Magnésique.)

* ITS solution, mixed with a sufficient quantity of muriate of ammonia, so that ammonia produces no precipitate of hydrate of magnesia (page 39), is sometimes used subsequently to an addition of ammonia, for detecting phosphoric acid, especially in

solutions which contain sulphuric acid at the same time (pages 262, 264).

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[1] The acid succinate of ammonia is in crystals, which are unalterable in the air, and may be used instead of the neutral succinate, by neutralising its solution ; for, without this precaution, the precipitate of persuccinate of iron would dissolve whilst washing.—ED.

8. CHROMATE OF POTASH.)

(*Chromate Potassique.*)

* SOLUTION of CHROMATE OF POTASH is used for precipitating several *metallic oxydes.*

* The *chromate of potash* of commerce may be contaminated by *sulphate of potash,* the presence of which may be detected by adding tartaric acid, or else oxalic acid and muriatic acid, and heating the whole; by which means the chromic acid of the chromate is converted into green oxyde of chromium, which remains dissolved in the acids (page 349), when, if the green solution contains any sulphuric acid, a solution of chloride of barium will produce a precipitate of sulphate of baryta[1]. If the *chromate of potash* contain any *nitrate of potash* it fuses upon ignited charcoal.

* The yellow neutral chromate of potash is not, however, so free from impurities as the BICHROMATE OF POTASH, which on that account is used in preference as a test.

9. IODIDE OF POTASSIUM.

(*Iodure Potassique.*)

* THE solution of IODIDE OF POTASSIUM is employed as a test for several metallic oxydes in the solutions of which it produces precipitates of a characteristic colour. I have, however, said on a former occasion (page 431), that *iodide of potassium* was not a very available re-agent.

* *Iodide of potassium* may be falsified by *chloride of potassium* or of *sodium,* or other metallic *chlorides,* which impurities may be detected by the methods indicated (page 431). If it contain any *iodate of potash* it may be detected as shown in page 432. If it be contaminated by any *carbonate of alkali* the addition of

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[1] Chromate of potash may be tested at once for sulphuric acid by nitrate of baryta and nitric acid. It is true that a precipitate of chromate of baryta would be formed; but chromate of baryta is soluble in free nitric acid, whilst sulphate of baryta is perfectly insoluble in it.—ED.

an acid will disengage carbonic acid, and it will not completely dissolve in alcohol.

10. BICARBONATE OF POTASH.

(*Bicarbonate Potassique.*)

* THE solution of BICARBONATE OF POTASH and likewise that of BICARBONATE OF SODA serve principally to distinguish *magnesia* from *alumina* (pages 40—45), and likewise *baryta, strontia,* and *lime* from *protoxyde of manganese,* &c.

* When *bicarbonate of potash* contains any *carbonate of potash* it deliquesces by exposure. If pure, its solution does not, in the cold, produce any precipitate in one of sulphate of magnesia.

11. SULPHATE OF POTASH.

(*Sulfate Potassique.*)

* SOLUTION of *sulphate of potash* is often used instead of *dilute sulphuric acid*[1] to distinguish *lime* from *baryta* (pages 34—24). It is used also to precipitate and detect *thorina* (page 51), *yttria* (page 53), *protoxyde of cerium* (page 55), and *zirconia* (page 59)[2].

* The *sulphate of potash* of commerce is often contaminated by various substances. If it contain *sulphate of zinc,* its solution, treated by hydrosulphuret of ammonia, yields a white precipitate of sulphuret of zinc, which has a blackish or brownish tinge if the salt contained traces of *sulphate of protoxyde of iron* or of *copper.* The presence of *sulphate of magnesia* is recognised by adding a solution of hydrate of potash to that of the salt, by which means a precipitate of magnesia is formed. If the salt

contain any *sulphate of lime*, a solution of binoxalate of potash produces a precipitate or a turbidness of oxalate of lime, especially if ammonia be further added. If the salt contains any *nitrate of potash* it fuses upon ignited charcoal. If mixed with *bisulphate of potash* the solution strongly reddens litmus paper[1].

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[1] It is often preferred to sulphuric acid, because it forms the same precipitates as dilute sulphuric acid, but being a neutral salt the neutrality of the solution operated upon is thus left undisturbed.—ED.

[2] *Sulphate of potash* is also often used as a test for tartaric acid, for which it is a better re-agent than carbonate or hydrate of potash, a slight excess of which is sufficient to prevent the formation of bitartrate of potash, which is the characteristic precipitate. Any other salt of potash may produce this precipitate of bitartrate, but *acetate of potash* deserves the preference, because bitartrate of potash is insoluble in free acetic acid, whilst, on the contrary, it is soluble in alkalies and in mineral acids.—ED.

12. SULPHATE OF LIME.

(*Sulfate Calcique.*)

* THE solution of *sulphate of lime* is used to recognise *oxalic acid* (page 387), and *paratartaric acid* (page 399), and likewise to distinguish *lime* from *baryta* and from *strontia* (page 35).

* The solution of *sulphate of lime* is prepared by putting the pulverised and pure salt in a flask with distilled water, agitating the whole and leaving the excess of the salt to deposit. For use, the clear supernatant liquid is poured off and replaced by distilled water, in order to have always a saturated solution in reserve[2].

13. LIME-WATER.

(*Eau de Chaux.*)

* LIME-WATER may be employed to precipitate *arsenious acid* (page 340), *carbonic acid* (page 383), and often also the solutions of the phosphates. It should render litmus paper strongly blue. If not carefully kept it will deposit most of its lime and become useless[3]. ¶

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[1] ACETATE OF POTASH should appear amongst this list of special re-agents as a test for *tartaric acid*. See the preceding note.

[2] The pure sulphate of lime may be obtained by pouring sulphuric acid upon a concentrated solution of chloride of calcium, and washing carefully the precipitate thus produced.—ED.

[3] Lime-water is made by pouring cold distilled water upon recently-prepared hydrate of lime, and leaving the whole to digest for some time, frequently agitating the mixture; after which the clear supernatant liquid is poured off and kept for use in well stoppered phials.—ED.

¶ BARYTA-WATER is a test which is often used instead of lime-water, for precipitating carbonic acid. Baryta-water precipitates all the alkaline earths from the solutions of their salts. Baryta-water may be substituted for the barytic salts for the detection of sulphuric acid.—ED.

14. CARBONATE OF BARYTA.

(*Carbonate Barytique.*)

* CARBONATE OF BARYTA is used for precipitating several oxydes and separating them from each other. It should be exempt from *alkaline* and *other salts*. Its purity may be tested by boiling a certain quantity of it in water, filtering and evaporating to dryness. No residuum should be left.

* When *carbonate of baryta* is not at hand, pure CARBONATE OF LIME may be used instead. *Lime*, however, does not separate from a liquor so promptly as baryta; owing to which, carbonate of baryta is preferable[1].

15. PERCHLORIDE OF GOLD.

(*Chlorure Aurique.*)

* THE neutral solution of chloride of gold is used as a test for *protoxyde of iron*, *protoxyde of tin*, and several acids which separate metallic gold from its solution.

16. NITRATE OF SUBOXYDE OF MERCURY.

(*Nitrate Mercureux.*)

* THE solution of SUBNITRATE OF MERCURY (Hg_2O+NO_5) is used to precipitate and recognise *gold*, *platinum*, and some other metals, and likewise to precipitate certain acids, especially many organic acids[2].

* If the solution contains *peroxyde of mercury* (HgO) along with the suboxyde, the whole of the mercury is not precipitated in the state of subchloride by addition of an excess of solution of chloride of sodium, and perchloride of mercury may still be found in the filtered liquid. When the salt is neutral, a white powder of subchloride of mercury (calomel) is obtained by

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[1] Carbonate of lime being used in muriatic acid solutions yields of course a solution of chloride of calcium, which filters with much more difficulty than chloride of barium, which is an additional reason for giving preference to carbonate of baryta. —ED.

[2] Subnitrate of mercury is also employed as a test for ammonia. See page 22.

triturating it in the dry state with an excess of chloride of sodium, and subsequently adding water; if, on the contrary, it is basic, a greenish powder is thus obtained, which is a mixture of subchloride and of protochloride of mercury (calomel and corrosive sublimate). In either case, the filtered liquid contains no mercury in solution.

17. CYANIDE OF MERCURY.

(*Cyanure Mercurique.*)

* CYANIDE OF MERCURY may be used to detect *palladium* (page 155), and in some cases *platinum* (page 150); the solution must not have a basic reaction.

18. PERCHLORIDE OF MERCURY, Hg Cl.

[CORROSIVE SUBLIMATE.]

(*Chlorure Mercurique.*)

* THE solution of PERCHLORIDE OF MERCURY may principally be employed for detecting *phosphorous* and *hypophosphorous acids* and their salts when they are mixed with *phosphoric acid*, or with *phosphates* (pages 273, 277). It may also be resorted to for the purpose of detecting the substances which are capable of reducing perchloride of mercury into subchloride of mercury, or into metallic mercury. Its behaviour with *phosphuretted hydrogen* and with *arseniuretted hydrogen* is very characteristic.

* *Perchloride of mercury* is pure if it volatilises without residuum when exposed to heat. It must also be completely soluble in water, in alcohol, and in ether.

19. SULPHATE OF COPPER.

(*Sulfate Cuivrique.*)

* SOLUTION of SULPHATE OF COPPER is sometimes used for the detection of arsenious acid (page 341). The commercial sulphate of copper may be used for that purpose, though it often contains small quantities of *protosulphate of iron*, and of *sulphate of zinc*.

20. PERCHLORIDE OF IRON.

(Chlorure Ferrique.)

* PERCHLORIDE OF IRON, or any other persalt of iron, such as SULPHATE OF PEROXYDE OF IRON[1] (*sulfate ferrique*), is especially used for detecting *acetic acid*[2], (page 413), and *formic acid* (page 415).

21. SULPHUROUS ACID.

(Acide Sulfureux.)

* THE aqueous solution of SULPHUROUS ACID, or that in alcohol in which the acid is more soluble than in water, seems more especially to precipitate *selenious acid* and *tellurious acid* from their solutions, and from that of their salts (pages 223—229); but it is also employed for the purpose of reducing certain metals, and of converting certain higher degrees into lower degrees of oxydisation. Yet for such a purpose it is better to use the solution of a sulphite of alkali, such as SULPHITE OF AMMONIA, or SULPHITE OF SODA. But with respect to the latter, it should be employed only in the solid state, or else it should be dissolved only a few minutes before using it.

* When the solution of *sulphurous acid* or of the *sulphites of alkalies* has not been carefully sheltered from the air, a certain quantity of *sulphuric acid* is always formed; owing to which, chloride of barium produces in its solution a white precipitate, insoluble in muriatic acid if the solution be one of sulphurous acid, and partly soluble in that acid, if the solution be one of a sulphite of alkali. In most cases, the presence of sulphuric acid does not interfere.

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[1] The salt is pure when not precipitated by ferricyanide of potassium, which otherwise would indicate the presence of a protosalt of iron. The solution of a persalt of iron used as a test must not contain any excess of acid. This is ascertained by pouring in the solution a drop of dilute ammonia, which will immediately produce a small precipitate of peroxide of iron; if by stirring the mixture the precipitate redissolves, there is an excess of acid.—ED.

[2] Another test for acetic acid is PROTOXYDE OF LEAD (see the note page 414), which yields with acetic acid a solution which re-acts upon test papers like an alkali. This test is characteristic.—ED.

* The best method to prepare sulphurous acid consists in heating concentrated sulphuric acid and coarsely pulverised charcoal together; the gas is then received in water, alcohol, ammonia, or a solution of carbonate of alkali.

22. PHOSPHOROUS ACID.

(*Acide Phosphoreux.*)

* PHOSPHOROUS ACID, or the compound of *phosphorous* and of *phosphoric acid*, which is produced by the spontaneous combustion of phosphorus in moist air, is often an excellent reducing agent.

23. BASIC SILICATE OF POTASH.

[LIQUOR SILICUM.]

(*Soussilicate Potassique.*)

* THE solution of the BASIC SILICATE OF POTASH is used to detect phosphoric acid in phosphate of alumina (page 265).

24. SULPHOCYANIDE OF POTASSIUM.

(*Sulphocyanure Potassique.*)

* THE solution of SULPHOCYANIDE OF POTASSIUM serves to detect the smallest traces of *peroxyde of iron* (page 490).

25. NITRATE OF POTASH.

(*Nitrate Potassique.*)

* IN the solid state, NITRATE OF POTASH is used to detect carbon in the substances which contain it, and for the purpose of oxydising a great number of metals and other substances. When employed for oxydising substances which contain sulphur, it must be perfectly free from *sulphate of potash*[1].

26. ZINC.

* METALLIC ZINC is used to precipitate several metals from their solutions. It is generally cast for the purpose, in the

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[1] Sulphate of potash may be detected by nitrate of baryta; and the presence of a chloride by nitrate of silver. If solution of carbonate of potash form a precipitate, the presence of metallic oxydes or of earthy matter are thereby indicated.—ED.

shape of small round bars, or in blades. The zinc of commerce is impure, and contains small quantities of *iron*, *cadmium*, *lead*, and other metals, the presence of which, however, is not very objectionable in most chemical analyses. It is better, however, when possible, to use pure distilled zinc[1].

27. IRON.

(*Fer.*)

* Metallic iron is used to precipitate small quantities of copper contained in solutions (page 121). A piece of polished sheet-iron, or the blade of a knife, or any other piece of malleable iron, may be used for this purpose.

28. COPPER.

(*Cuivre.*)

* Metallic copper is sometimes used in the state of copper plate to recognise *suboxyde of mercury* (page 134), and *peroxyde of mercury* (page 139), sometimes also in the state of copper turnings or trimmings, to detect *nitric acid.*

29. GOLD.

(*Or.*)

* Gold-leaf serves to detect *nitric acid, nitrous acid, chlorine,* and *muriatic acid.* With tin it is sometimes employed to detect small quantities of mercury (page 142).

30. PEROXYDE OF MANGANESE.

(*Suroxyde de Manganèse.*)

* Peroxyde of manganese, and very often *red lead* or *brown oxyde of lead* (*suroxyde plombeux* or *suroxyde plombique*) in its

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[1] An impurity generally found in zinc is arsenic, the smallest trace of which renders it, of course, altogether unfit for Marsh's apparatus. For reasons which I have given in note (page 525) the pure distilled zinc should not be melted in an iron spoon or other metallic utensil, for the purpose of casting it into bars, since it would thereby be contaminated. It is best to melt it in a hessian crucible, and to cast it in moulds of plaster of Paris or of chalk.—Ed.

stead, are employed to detect *muriatic acid* and most *metallic chlorides*.

31. INDIGO.

(*Indigo.*)

* THE solution of indigo in concentrated and fuming sulphuric acid is employed as a test for *nitric acid* [1].

32. STARCH.

(*Amidon.*)

* STARCH is used to detect iodine and the metallic iodides [2].

33. ETHER.

* ETHER is used principally to detect *bromine.* It is also used as a solvent, and as a precipitating agent.

34. INFUSION OF GALLS.

(*Infusion de Noix de Galles.*)

* INFUSION of galls may be used in some cases for the detection of small quantities of *peroxyde of iron* in solutions. It may likewise serve as a test for several other metallic oxydes, especially *titanic acid* (page 295), and *tantalic acid.* It is obtained by digesting coarsely pulverised gall-nuts into alcohol diluted with an equal quantity of cold water [3].

* The following addition by E. Peligot is found in the French edition :—

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[1] The solution of sulphate of indigo is further employed, as may have been seen, as a test for *chlorine* and the *nitrates;* in the latter case, the nitrate must first be decomposed by sulphuric acid, for nitric acid must be in a free state to destroy the blue colour of the indigo solution.—ED.

[2] Starch is to be used in the state of thin mucilage, which is prepared by rubbing common starch with cold water, and heating the mixture to the boiling point, taking care to stir all the while to prevent burning. Mucilage of starch is always to be used cold. Strips of paper dipped in this mucilage, and carefully dried, may be used as test-paper for iodine, in the same way as the ordinary test-papers.—ED.

[3] In organic analysis, *infusion of galls* is also used as a test for *quinine* and for *gelatine.*—ED.

"To these re-agents may be added

ANTIMONIATE OF POTASH.

(*Antimoniate Potassique.*)

Which is prepared by fusing antimonic acid with an excess of potash. The solution of this salt forms, according to Frémy, a good re-agent to distinguish and even to separate *soda* from *potash*. Antimoniate added to an aqueous solution of a salt of soda forms a crystalline and insoluble precipitate of antimoniate of soda; by this means $\frac{1}{350}$ of a salt of soda may be clearly detected.

"The precipitate requires a few seconds stirring for its production"[1].—E. P.

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* Amongst the number of the re-agents which cannot be dispensed with must be placed also those which are used with the blow-pipe; for even in analysis in the humid way, the blow-pipe must often be resorted to. Berzelius having detailed in his Treatise the re-agents which are to be used in these assays, I beg to refer the reader to that work, which will enable me to abridge the description of the use of the blow-pipe in qualitative analysis.

* We may only remark here, that in most blow-pipe assays there is no occasion for more than three dry re-agents, namely:—

* 1. DEHYDRATED CARBONATE OF SODA.

It is necessary that this salt be very pure, and free from *sulphate*

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[1] If the solution be somewhat dilute, some time must elapse for its production; if concentrated, it takes place immediately. It is, however, necessary to remark here, in reference to this re-agent, that though antimoniate of soda is very difficultly soluble in water, it is not altogether insoluble therein; wherefore the solution thus tested for soda must not be too dilute; and further, as antimoniate of potash is decomposed by all acids, even by carbonic acid, which would precipitate a biantimoniate of potash, the acid should be neutralised with *potash*, or *carbonate of potash*, and not by *ammonia*, because the *salts of ammonia* are also precipitated by antimoniate of potash; and in neutralising with *carbonate of potash* a large excess of this salt should be avoided, because antimoniate of soda is soluble in alkaline salts of potash. The solution of carbonate of potash should therefore be cautiously added until the solution be rendered very feebly alkaline. If too much carbonate of potash has been used, or if the liquor originally contains it, muriatic acid must be added to neutralise it. The absence of all other earths and metallic oxydes must be ascertained before testing for soda by antimoniate of potash.—Ed.

of soda especially. Its purity may be tested in the manner mentioned before (page 547). In blow-pipe experiments only, very small quantities of soda or of other re-agents are used. Pure *carbonate of soda* may be obtained by slightly calcining the bicarbonate of soda, or else the bicarbonate itself may at once be used. A small quantity of *chloride of sodium* is not objectionable in most cases.

* *Carbonate of soda* is employed to reduce certain metallic oxydes or their salts, and for obtaining the metal of the chlorides, bromides, and iodides; or else to see whether the metallic oxydes, being heated in conjunction with carbonate of soda, will fuse or flux with it or not; by which means the various metallic oxydes may be distinguished from each other[1].

2. PHOSPHATE OF SODA AND AMMONIA.

[MICROCOSMIC SALT.]

[*Phosphate Ammonico-sodique.*]

(*Sel de Phosphore.*)

* THIS salt, either prepared from urine or from phosphate of soda and sal ammoniac, ordinarily contains a small quantity of *chloride of sodium.* In most cases the presence of this impurity does not interfere in blow-pipe analysis; when, however, the operator is obliged to employ microcosmic salt with protoxyde of copper for the purpose of detecting the presence of metallic chlorides, bromides, and iodides (pages 424, 430, 435), it is necessary that it should be free from all admixture with *chloride of sodium,* the presence of which may be detected by dissolving the salt and testing by nitric acid and nitrate of silver, which will then yield a precipitate of chloride of silver.

* Neither should *microcosmic salt* contain an excess of *phosphate of soda.* This is ascertained by fusing the salt before the blow-pipe upon charcoal, by which means a clear, colourless, perfectly transparent bead will be obtained, if there be no excess of

phosphate of soda, whilst if the reverse be the case, the bead after cooling is not limpid.

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[1] A mixture of about equal parts of *carbonate of soda* and *cyanide of potassium* is, however, a much more powerful reducing agent than *carbonate of soda* alone.—ED.

* *Microcosmic salt* dissolves by fusion nearly all substances; a few only which have acid properties resist its action. When *microcosmic salt* is heated, the ammonia and the water of crystallisation escape, and it acts then by the free phosphoric acid which it contains.

3. BORAX.

* THE BORAX of commerce is generally pure, and may be used in blow-pipe analysis[1]. When prepared from tinkal it contains a small quantity of organic matter, owing to which it yields after fusion a greyish or blackish bead, which however becomes colourless by continuing the fire. Borax, to be fit for blow-pipe experiments, must, by being dissolved in water, yield a solution which, after addition of nitric acid, must not be rendered turbid by solution of nitrate of silver, nor by that of chloride of barium [or nitrate of baryta[2]]. It dissolves by fusion all oxydised substances, whether they act as bases or as acids.

* Besides these principal re-agents a few others are employed in particular cases, and only for special substances; they are:—

1. BORACIC ACID.

(*Acide Borique.*)

* BORACIC ACID is used with *iron* to detect *phosphoric acid* (page 270).

2. SOLUTION OF NITRATE OF COBALT.

(*Nitrate Cobaltique.*)

* SOLUTION OF NITRATE OF COBALT must be kept in a glass-stoppered phial, the stopper of which is terminated internally by a long glass tube drawn to a point, by which means a single drop of the solution may be extracted from the mass[3]. This

re-agent is seldom used for any other purpose than as a test for *magnesia* (page 42) and alumina (page 47). It is employed also, but the reaction is less certain, as a test for *oxyde of zinc* (page 73) and a few other oxydes.

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[1] It is, however, advisable to recrystallise it.—ED.

[2] Neither must solution of *carbonate of potash* or of *soda* render the aqueous solution of borax turbid.—ED.

[3] An exceedingly minute quantity of this or any other fluid re-agent may be added

* The solution of *nitrate of cobalt* must be prepared by dissolving pure cobalt in pure nitric acid; an excess of *free acid* is no objection. Generally, the presence of *arsenic* or *arsenious acid* is of no consequence, but it must especially be free from *fixed alkalies;* and when an oxyde of cobalt, which has been precipitated from its solution by *hydrate of potash,* is employed, it must be carefully washed. Neither must the solution contain any *peroxyde of iron* or other oxydes.

* Instead of a solution of *nitrate of cobalt,* OXALATE OF COBALT in powder may be used. The substance under examination must then be mingled with a little water and *oxalate of cobalt,* and the substance must be heated longer than when *nitrate of cobalt* is employed.

3. SOLUTION OF NITRATE OF NICKEL.

(*Nitrate Nicolique.*)

* A SOLUTION of NITRATE OF NICKEL or one of OXALATE OF NICKEL are used to distinguish *soda* from *potash* (page 7). It is necessary that the nickel be perfectly free from cobalt; this is ascertained in the manner described (page 5).

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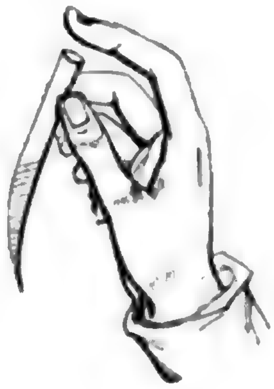
to the extent of one drop, half, or a quarter of a drop, or even less by means of a *pipette,* which I make from the neck of a broken retort. It is therefore a conical tube drawn to a point as represented in the figure. By plunging the tube in the phial containing the re-agent, a certain quantity of it rises spontaneously in it, or may be sucked up, and by putting the tip of the finger on the upper extremity the contents are thereby pushed out in very minute drops.—ED.



4. PROTOXYDE OF COPPER.

(*Oxyde Cuivrique.*)

* THE purest oxyde is obtained by exposing nitrate of copper to a red heat. It is employed for detecting ***chlorine, bromine, iodine*** (page 424); but in order to be fit for this use the oxyde must be perfectly free from chlorine, and the copper employed to prepare the nitrate must have been dissolved in pure nitric acid.

5. PULVERISED FLUORSPAR.

(*Spath-fluor pulvérisé.*)

* IT is used for detecting ***sulphate of baryta*** (page 28), of ***strontia*** (page 33), and of ***lime*** (page 38); for these are the only substances which can fuse with ***fluorspar*** into a colourless bead, which on cooling becomes milk-white.

6. TIN.

(*Étain.*)

* TIN is resorted to for the purpose of reducing the lower degrees of oxydisation into still lower degrees of oxydisation, or into the metallic state. The best are ***tin shavings,*** which are obtained by scraping a bar of tin with a knife, or else tin-foil.

7. IRON.

(*Fer.*)

* PIANOFORTE steel wire, No. 7 or 8, is used to detect ***phosphoric acid*** (page 270).

8. BISULPHATE OF POTASH.

(*Bisulphate Potassique.*)

* THIS substance serves to detect ***boracic acid*** in the ***borates*** (page 282), ***bromine*** (page 429), ***iodine*** (page 435).

9. SILICIC ACID.

(*Acide Silicique.*)

* THE best is to employ it in a state of extreme division, as it is obtained from the analysis of siliciferous minerals. It serves to detect ***sulphuric acid*** (page 204), and in general the substances which contain ***sulphur.***

CHAPTER II.

APPARATUS.

* The operations of qualitative analysis require, for the most part, a small number only of exceedingly simple apparatus and utensils, which may be easily procured.

* The most indispensable of these articles for operating in the humid way, are small glasses, in which the substances under examination may be dissolved, or else in which the solutions of substances may be tested by submitting them to the action of the re-agents. The glasses ordinarily employed are similar to those called champagne glasses[1]. It is impossible, however, to heat the liquor contained in such glasses, which is an inconvenience, because it is necessary to apply heat in almost every case of qualitative analysis; wherefore it is preferable to use cylindrical glasses, which may easily be made with tubes of white glass. For this purpose glass tubes must be chosen not too thick, and they are to be cut in lengths double that which it is intended that the test tube should have, after which they are

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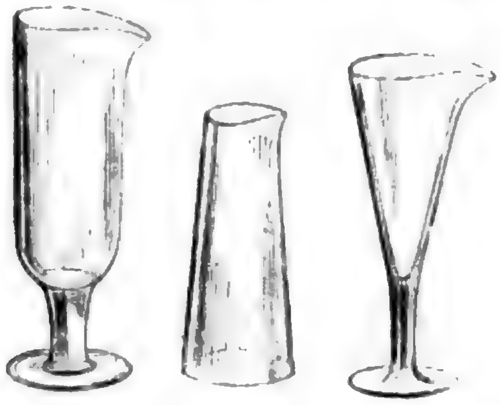
[1] The best forms of test glasses are here given. The middle one, known under

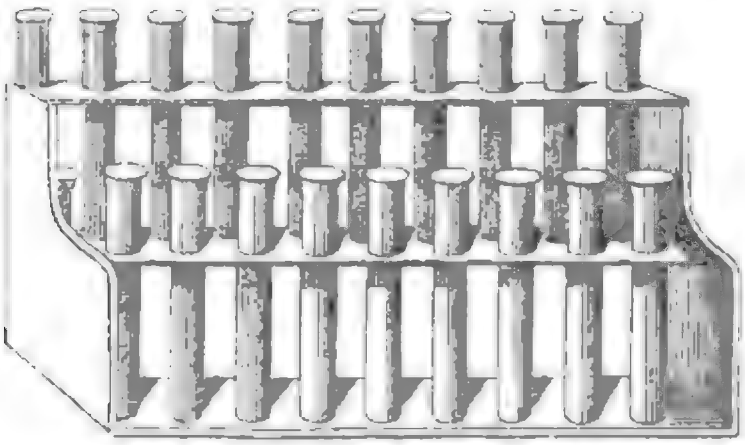


the name of Philipp's precipitating glass, is exceedingly convenient for allowing precipitates to subside. The two other forms are best adapted to testing.—Ed.

each to be heated in the middle by means of the enameller's blow-pipe, and when the glass has softened, the extremities are to be drawn, by which means two tubes are obtained of an equal length, and almost closed at one end. That almost closed end is to be well fused, and then gently blown, so as to render it hemispherical. The upper part or open end of the tube may now be heated likewise before the enameller's blow-pipe, in order to turn the brim slightly over for the purpose of facilitating the transferring of liquids. The most convenient size for test tubes is about five inches in length, by three quarters of an inch in diameter[1].

* Solutions, as well as their precipitates, may be readily heated, or even boiled in such tubes, but when insoluble substances are boiled therein with a liquid, in order to prevent their boiling too violently, it is necessary that the closed end of the tube be of a uniform thickness. It often happens by boiling in these tubes liquids in the midst of which an insoluble precipitate has been formed, that the liquor boils up so violently, that a great portion of the liquid and of the precipitate is projected out of the tube almost explosively, which is not even without danger to the operator. Such glasses must not be employed except for experiments in which it is not necessary to apply heat. Whenever it is necessary to boil a liquid, the orifice of the tube must be inclined in such a direction that the portions which might be projected may not prove hurtful.

* About twenty such tubes are required, which may be placed



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[1] Test tubes should be made of thin glass and well annealed, so that boiling hot liquids may be poured into them without fear of cracking them.—Ed.

in two tiers, in a frame, as in the preceding page:—The tubes of the lower tier are a little larger and longer than those of the upper one.

* As the phenomena which the re-agents determine in the solutions of the substances under examination are not always produced immediately, but, on the contrary, require a certain lapse of time to become manifest, the solution, after mixing with the re-agent, should be left at rest, and in order to avoid committing errors, the name of the re-agent, added to the solution in the glass, must be written upon gummed paper, and pasted upon it[1].

* It is advisable to have a separate apparatus for precipitations by means of the aqueous solution of sulphuretted hydrogen, or of hydrosulphuret of ammonia, because it is absolutely necessary to perform such experiments under a strong draught of air, in order to get rid of the noxious vapours. This precaution should never be neglected, not only because the odour of sulphuretted hydrogen is exceedingly disagreeable, but also because it may prove extremely injurious to health. The experiments with the other re-agents may be conducted in a common room.

* Instead of these glass tubes, small mattrasses may be used for boiling liquids. The explosive boiling above alluded to is less liable to take place in such utensils.

* Glass funnels are also required, and likewise paper filters, in order to collect precipitates, and a certain number of ordinary glasses or beakers of various sizes.

* The other necessary utensils are, a small spirit-lamp with ground glass cover, and a large spirit-lamp with circular wick (Berzelius spirit-lamp), for cases in which a more intense heat is required; a strip of platinum foil; a small and thin platinum crucible capable of holding about 500 grains of water; several small porcelain crucibles of the same size as above; several porcelain evaporating dishes; a small agate mortar with its pestle;

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[1] Common ink should not be used for the purpose, as it is liable to be obliterated or discharged by acids, &c. It is better to employ a lead pencil, but black chalk is best.—Ed.

several small glass tubes; a syringe bottle; a few tubulated bottles for disengaging sulphuretted hydrogen, carbonic acid, &c.[1]; a few watch-glasses. A few glass retorts and receivers are also required in some cases. The description of all these utensils may be found in Berzelius' treatise, to which the reader is referred[2].

* I have said (page 574) that the blow-pipe is an indispensable instrument in most operations of qualitative analysis. Both the instruments and the utensils which its use requires are fully described in Berzelius' treatise.

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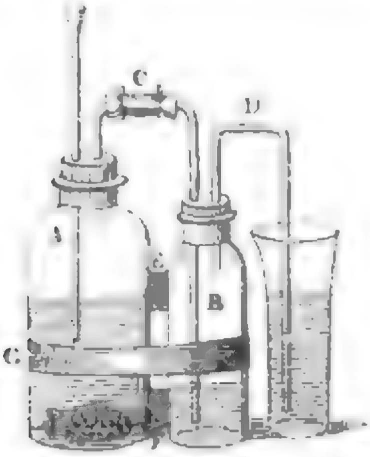
[1] Ordinary bottles, provided with sound corks fitting tight, and which may be perforated with the necessary number of holes for the reception of the tubes of disengagement, funnel, &c., answer the same purpose. See fig. of note 2, page 549. The apparatus there described has, however, the inconvenience of not being easily portable, and of requiring to be mounted every time it is wanted. To remedy this I use in my laboratory the following contrivance:—



A is the bottle containing the protosulphuret of iron, water, and sulphuric acid, and provided with funnel and disengagement tube as usual, the latter plunging in the water of a smaller bottle B, from which a disengagement tube D nearly as high as that of bottle A issues, so as to lead the gas disengaged in a beaker or other vessel containing the liquor to be operated upon—but the first disengagement tube C is in two pieces united by Indian rubber, and the bottles A B are connected together by a strong band of sulphurised Indian rubber or of gutta-percha G, so that the two bottles may be lifted at once as if it were one bottle, wedges of cork E E being forced between the two bottles so as to keep the strip of Indian rubber G and the tube C properly adjusted.—Ed.

[2] Berzelius's admirable work has never been translated into English! The apparatus and utensils alluded to may be procured in London, at Messrs. Charles Button, 146, Holborn Bars; Messrs. Horne, Newgate Street; Willats, Cheapside; Knight, Foster Lane, Cheapside; and at most operative and manufacturing chemists in the kingdom.—Ed.

CHAPTER III.

GENERAL RULES TO BE FOLLOWED IN QUALITATIVE ANALYSIS.

* We shall speak here of the qualitative analysis of the solid inorganic substances only. The course to be adopted for that of gaseous bodies will be indicated further on.

* It is always difficult for a beginner to determine upon what quantity of the substance to be qualitatively analysed he should operate. It is not advisable, even when the substance to be analysed is plentiful, to operate upon too large a quantity, though the operation is thereby greatly facilitated, since it is then possible to take different portions of that substance for the purpose of determining the various constituent principles, which cannot be done when only a small quantity of it can be disposed of. At all events, the analyst must never experiment upon the whole of the substance, but should always reserve part of it, except in case of absolute necessity. This precaution should never be neglected, even when the quantity of the substance to be examined is very small. The most convenient quantity for a beginner to operate upon, is two or three grammes (from 30 to 50 grains), when there is plenty of the substance.

* Whether the substance to be examined is in abundant or in small quantity, it is always advisable to take a very small portion of it for the purpose of ascertaining whether it is composed of inorganic substances only, or whether, on the contrary, it does not contain some organic matter. This may be ascertained in various ways, but the best for a beginner is the following:—If

the substance be in powder, take a small portion of it with the point of a knife, or if in compact masses, break off a few grains of it, and introduce these portions in a white glass tube[1], closed at one end, of about two inches in length, and three or four-eighths of an inch in diameter. The closed end of this tube may be slightly blown, but very slightly, as the glass must not be too thin at that point. The closed end containing the substance to be tested is then heated in the flame of a small spirit-lamp, during which operation the tube must be held up at a moderate angle, but not in a perpendicular nor a horizontal position. Most organic substances become black by exposure to heat when the air is not freely admitted, and at the same time, and in most cases, though not always, the ordinary products of the distillation of organic substances are formed, namely, empyreumatic oil and water. There are, however, cases which do not exhibit these phenomena, although organic matter is present; but the number of such cases is very limited, and when the organic substance is of a volatile nature, it may be completely evaporated without turning black by charring, and this may happen even though the organic matter be mixed or combined with fixed inorganic substances. Yet the presence of a fixed inorganic matter often determines the carbonisation of the volatile organic element. Such is the case, for example, with the organic acids, which in the free state, and when they contain water, may be completely volatilised without decomposition, but which, when combined with fixed inorganic bases, are decomposed, and charred by exposure to heat.

* When the substance contains an organic body, the operator may at the same time ascertain whether it contains nitrogen. This may be done by holding a strip of reddened litmus paper, previously moistened, at the orifice of the glass tube, and at a sufficient distance of the heated point, in order to prevent its being destroyed by the heat. If the organic substance contains

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[1] The glass of the tube must be free from lead, else it will turn black by exposure to heat, and thus simulate the presence of organic matter. It is always best, if possible, to reduce the substance into powder before putting it in the tube.—Ed.

any nitrogen, however little, it will yield *ammonia,* which will turn the strip of reddened paper blue. If the proportion of nitrogen be considerable, a white cloud is produced by holding a glass rod moistened with muriatic acid at the orifice of the tube (page 22).

* When the substance contains no organic matter, the above experiment may also indicate whether it contains any *water,* or other *volatile matter.* If water be present, it condenses into drops on the cold sides of the heated tube[1]. If a narrow strip of litmus paper be now introduced in the tube, so as to make it touch the condensed water, the operator may see whether it has an alkaline or an acid reaction. An alkaline reaction of the water indicates in some cases the presence of *ammonia,* but it may be due also to the substance under examination, which may be susceptible of an alkaline reaction, and which may have been mechanically thrown up in the upper part of the tube.

* The application of heat alone may thus volatilise not only the *water,* but also the *ammoniacal salts* contained in the substance in question. Amongst the ammoniacal salts a few only are not thus decomposed, but in that case a *white sublimate* is produced, which deposits in the colder parts of the glass tube; in most cases, however, a temperature much higher than that at which the water volatilises is required to produce this white precipitate. The presence of ammonia in the sublimate is very easily detected (page 22).

* Heat volatilises also the salts which contain *mercury,* amongst which *perchloride* and *subchloride of mercury* are the only ones which are not thus decomposed. In most cases the mercury of such salts is reduced, and is deposited in the metallic state in the colder portions of the tube.

* Various other substances are volatilised by heat, either in the gaseous, or in the liquid, or solid state; such is the case with

the *volatile acids, sulphur,* some *metallic sulphurets, selenium,* and some *metallic seleniurets,* certain *volatile oxydes;* and lastly, *mercury,* and some other *volatile metals.*

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[1] If the substance under examination contains an organic body and also water, the latter will evaporate long before the charring of the organic matter has taken place, and condense on the sides of the tube.—Ed.

* The analyst who can manage the blow-pipe may perform these experiments upon much smaller quantities. Small glass tubes are used for the purpose, of a very small diameter, closed at one end, and in which the substance may be heated by the flame of alcohol urged by the blow-pipe. A temperature may thus be obtained much more intense than even by heating larger quantities in large tubes in the flame of a spirit-lamp with circular wick. The presence of organic substances may be detected by the same reactions as have been indicated just above; but that of volatile substances is at the same time much more readily discovered, especially those which require a high temperature for their volatilisation. I shall give further on a list of the volatile substances which may thus be detected by the blow-pipe.

* When the object of the analysis is merely to know whether the substance under examination is of an organic nature, or whether it contains any organic matter, the following summary process is frequently resorted to, which consists in heating it before the blow-pipe upon a charcoal support, or even upon a platinum foil in the flame of the spirit-lamp. In most cases this method answers perfectly well, but, except the operator be well used to it, it is less commodious for the purpose of detecting small quantities of organic matter.

* When, however, the object in view is to ascertain whether an organic substance contains any fixed inorganic constituents, the easiest and most convenient way is to heat a small quantity of it upon platinum foil by means of the spirit-lamp, or of the blow-pipe, until it is entirely carbonised, and then to burn the carbon completely off by means of the intense heat of the flame of the blow-pipe playing upon that portion of the foil on which the carbonised mass rests. One may thus easily discover very small portions of inorganic matter in very large quantities of organic substances, the inorganic matters

remaining in the state of ashes. Yet the incineration of the carbonised mass often requires care, because a great number of inorganic bodies, which are generally looked upon as fixed bodies, may be volatilised by a strong heat in contact with the air; such are, for example, *chloride of potassium*, of *sodium*, of *lead*, and *a few other chlorides*[1]. If the substance in question contain easily reducible metallic oxydes, it often happens that the platinum foil is strongly attacked by the reduced metal. In such cases small plates of mica may be used[2]. Certain organic substances, especially those containing nitrogen, readily fuse under the first impression of heat, and yield a charcoal which it is difficult to incinerate, but which, however, may ultimately be ignited upon a foil of platinum by means of the blow-pipe.

* Inorganic substances are often materially altered by exposure to heat, and it may even happen that they will turn black or blackish because they accidentally contain organic substances, or through other reasons. But when, as a counter-proof, a small quantity of the organic substance is heated in the same way, the phenomena are so manifestly different in most cases, that it is very rare that the presence or absence of organic matter as an essential constituent of the substance in question can remain a matter of doubt. Should, however, such a circumstance present itself, the operator should fuse a little nitrate of potash in a porcelain crucible, and a small portion of the substance under trial is to be projected into the fused salt. All organic substances, almost without exception, deflagrate when thrown into fused nitre, but not exclusively so, the same effect being produced by the combustible inorganic substances, for example, *sulphur*, the *metallic sulphurets*, a few *metals*, and certain *metalloïds* in a state of extreme division. Yet the property of turning black by heat and of deflagrating when

thrown in fused nitre is not met with simultaneously in any but an organic substance.

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[1] It is also necessary to bear in mind that chloride of potassium and of sodium decrepitate when heated. Chloride of lead readily fuses, and then emits thick fumes, because it partly evaporates, leaving a yellow residuum, which is a basic chloride of lead.—Ed.

[2] Or else a small porcelain crucible.—Ed.

* The means of determining the nature of the organic substance, after its existence has been demonstrated as above, does not form part of the plan of this work. Nor is the analytical chemistry of organic substances sufficiently advanced to enable me to do it in this manual, but when the combination under examination contains inorganic and organic substances, they may be determined, especially if the former be of a fixed nature.

* The presence of organic substances, especially of those which in the pure state cannot be volatilised by heat without undergoing decomposition, modifies in various ways the behaviour of a great number of re-agents towards inorganic substances. I have shown in the First Part of this volume, in reference to the inorganic oxydes, what are the changes which the presence of organic bodies produces in the phenomena resulting from their contact with the re-agents, and if I beg to call the reader's attention again to this fact, it is because the presence of organic substances prevents many oxydes from being precipitated from the solutions by alkalies, by which they would otherwise be completely precipitated. Even when, which is very often the case with a great number of oxydes, the presence of an organic substance does not prevent their detection and precipitation, it is, nevertheless, very inconvenient in many other respects in qualitative analysis. Many organic substances, for example, sugar, gum, and the like, render the filtering of liquids and the separation of the precipitates produced by the re-agents an extremely tedious and difficult operation. Very often also their presence renders it impossible to collect on a filter the metallic sulphurets which sulphuretted hydrogen and hydrosulphuret of ammonia may have produced in solutions of metallic oxydes. Frequently these substances remain for a very long time in suspension without subsiding. The same is the case with the precipitates of sulphate of baryta, sulphate of lead, &c. The presence of some non-volatile organic acids, for example, tartaric acid, may render it difficult to collect on a filter recently precipitated

metallic sulphurets, though much less than is the case with sugar, gum, and other organic substances.

* The best thing to be done in most cases, for the purpose of finding the constituent principles of an inorganic body mixed or combined with organic substances, is to destroy the latter. The easiest way of effecting this, in most cases, is by ignition; and the best way of doing it consists in heating a small quantity of the substance in a small platinum crucible, by means of the flame of a spirit-lamp with circular wick. The crucible should be placed obliquely, with the cover so placed as to close only about three-fourths of the mouth of the crucible. The access of the air into the crucible is facilitated by putting a thin strip of sheet-iron in the uncovered part of the crucible, and stirring the red-hot substance from time to time with a platinum wire.

* If the substance under examination contain metallic oxydes easily reducible by charcoal, the combustion of the organic matter should not take place in a platinum crucible, because it would thereby be completely spoiled. The operation should then take place in a porcelain crucible, which is sometimes more difficult, because it is impossible to heat such a vessel to the requisite temperature by means of a spirit-lamp.

* When the experiment takes place with large quantities, a hessian crucible may often be employed, and the heat applied by means of a charcoal fire. When the substance contains oxydes which are easily reducible, the organic substance may frequently be oxydised by means of nitric acid or aqua regia, which however gives rise to the production of other substances the presence of which is quite as troublesome. This effect does not take place when the organic substance is oxydised by means of nitrate of potash, which on that account should often be preferred to nitric acid or aqua regia; it is only necessary to act with circumspection, and not to deflagrate too large portions of nitre at a time. It is best, therefore, to mix the substance to be oxydised with pulverised nitre, to fuse only small quantities of the mixture at a time in a porcelain crucible upon the flame of

the spirit-lamp, and to add a fresh quantity only after the complete oxydisation of the preceding one. Of course, in the subsequent examination of the substance which has been submitted to this treatment, regard must be had to the potash, carbonic acid, and a greater or less quantity of nitric and nitrous acids, which have thus been introduced.

CHAPTER IV.

COURSE OF BLOW-PIPE OPERATIONS.

* In the qualitative analysis of complex substances the blow-pipe cannot be dispensed with, because certain bodies, especially several metallic oxydes, are thus more easily and accurately recognised than in the humid way, especially upon small quantities. We should not advise to trust exclusively to the blow-pipe for the qualitative examination of a substance, especially if it contain several constituent principles. It is true that the operation is more readily successful with less complex compounds, but even then some of the constituent principles, often of an essential nature, may thus be overlooked, because a great many substances do not produce very distinct phenomena when treated in the dry way before the blow-pipe; whilst, on ther other hand, some substances react so powerfully as to eclipse the reactions of the other bodies.

* The operator, however, who is familiar with the use of the blow-pipe, begins by submitting to its action, if not all substances, at least most of them; and in order to be sure that he has overlooked nothing, he subsequently proceeds to analyse them in the humid way. Sometimes, however, the experiment is not carried further than the examination with the blow-pipe, especially when the object is merely to ascertain the presence of substances which may be detected in this manner. This is frequently the case in analysis for technical purposes. Wherefore I have thought fit to indicate the course to be adopted for

the detection of the presence of those constituent bodies which may be accurately recognised by the blow-pipe.

* I will suppose the reader acquainted with the construction of the blow-pipe, its form, and the parts of which it is composed, the apparatus to be used with the blow-pipe, and the precaution to be taken whilst using the instrument. All these points have been developed in a complete manner by Berzelius in his treatise on the blow-pipe, to which work the reader is referred.

* The first operation should take place on very small portions of the substance under examination, and it is only subsequently that the substance is dissolved in the fluxes.

* The course to be adopted for the detection of the constituent parts of an unknown substance by means of the blow-pipe alone, is as follows:—

FIRST OPERATION.

THE substance is to be heated in a small glass matras, or in a glass tube sealed at one end. At first only the flame of a small spirit-lamp is applied, the object of this operation being, as I have said (page 583), to ascertain whether the substance contains any VOLATILE PRINCIPLES, or whether any ORGANIC MATTER forms part of the compound. The heat is subsequently increased by urging the flame of the spirit-lamp with the blow-pipe. The substances which in this operation may be volatilised without decomposition, or after having been decomposed, are principally the following:—

* WATER may be contained in the substance under examination, either as an essential constituent part, or as water of decrepitation. A little experience soon enables the operator to judge, from the quantity which condenses on the cold sides of the tube, whether it is an essential constituent portion of the substance, or whether it is only hygroscopic water. The operator must likewise examine whether the liquid thus obtained has an alkaline or an acid reaction, or behaves like pure water towards litmus paper. If it have an alkaline reaction, it can be owing to nothing else but *ammonia*, the presence of which may be

recognised by the white clouds which a glass rod moistened with muriatic acid, will produce when held over the said liquid.

* VOLATILE ACIDS *in the gaseous or in the liquid state.* The acid salts of the acids which, in the pure or in the aqueous state, are volatile, being heated in a small glass matrass, by means of the blow-pipe or of the flame of the spirit-lamp, lose the excess of acid, which then strongly reddens blue litmus paper previously moistened and introduced into the neck of the matrass. A few only of the neutral salts of these volatile acids are decomposed when thus heated in a small glass flask; such is especially the case with a great number of neutral NITRATES, which fill up the flask with red fumes of nitrous acid. It is safe to treat the nitrates by *bisulphate of potash,* in the manner which will be indicated further on[1], because when thus treated, they all react in the manner just alluded to. The acids of the HYPOSULPHATES and HYPOSULPHITES are likewise decomposed when these salts are heated in the small glass flask, and may be recognised as such by the odour of sulphurous acid evolved (page 208). In a few cases hydrofluoric acid may likewise be expelled from the COMBINATIONS OF FLUORINE, by the application of heat alone; such is the case when the compound contains at the same time a little water (page 441).

* SULPHUR and some METALLIC SULPHURETS.—From the substance under examination a sublimate of *sulphur* may take place when this body is either merely in the state of mixture, or when the substance contains *metallic sulphurets* which are susceptible of abandoning part of their sulphur when heated out of the contact of the air. In this case the sulphur sublimes in the form of drops, which are reddish-brown whilst hot, but which, on cooling, assume the characteristic yellow colour of sulphur. The *metallic sulphurets* which, being treated in this manner, are reduced by the loss of part of this sulphur into a lower degree of sulphuration, have been enumerated (page 476);

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[1] See page 598.—ED.

but there are several others which may lose a certain quantity of their sulphur, which condenses on the cold sides of the tube or small flask, because, when thus heated, it is impossible to shelter them altogether from the contact of the air; in consequence of which the oxygen of the air expels a small portion of the sulphur which they contain. The number of the metallic sulphurets which sublime without decomposition, is very inconsiderable, and is limited to SULPHURET OF MERCURY, which acquires a red colour by trituration, and the SULPHURETS OF ARSENIC, which might be easily mistaken by an inexperienced operator for pure sulphur; but the presence of arsenic may be easily detected therein by the methods which have been indicated (page 352)[1].

* SELENIUM and some METALLIC SELENIURETS.—Selenium may be sublimed in the same circumstances as sulphur, either because some selenium is actually mixed with the substance, or because the latter contains metallic seleniurets rich in selenium. The selenium condenses in small quantity under the form of a reddish sublimate; if in more considerable quantity the sublimate has a black colour, but yields a deep-red powder by trituration, and which may be recognised by the odour of its fumes, &c. (page 495). Amongst the metallic seleniurets those of MERCURY and of ARSENIC are volatilisable, yet the latter undergoes slight decomposition during the experiment.

* VOLATILE METALS.—They are principally ARSENIC, MERCURY, CADMIUM, TELLURIUM, all of which have a metallic lustre and a black or grey colour.

ARSENIC sublimes both when it forms an essential portion of the substance under examination, and when this substance consists of metallic arseniurets, containing a large quantity of arsenic, and susceptible of being converted by heat into less arseniетted arseniurets, or into arseniurets in which the arsenic has only a weak affinity for the other metal. Among the first of this class we may name the alloys of *arsenic* with *nickel* (arsenical nickel), with *cobalt* (grey cobalt), with *iron*, &c. The alloys of *arsenic* with *antimony* may be named as examples of the second class. A few *arsenites* yield likewise metallic arsenic when heated out of the contact of the air. It is exceedingly easy to detect the presence of the most minute traces of a sublimate of metallic arsenic.

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[1] This yellow sublimate may at once be identified as sulphur, if it be such, by scraping a portion off the tube with a knife or strip of platinum foil, and placing it in or close to the flame of the spirit-lamp, when it will immediately ignite and burn with the lambent blue flame of sulphur, and emit the odour of sulphurous acid.—ED.

* MERCURY may be sublimed from most of its compounds, and it is more easily identified than any other metal. If the quantity be inconsiderable, it often yields a grey sublimate only, but in which globules of mercury may be distinctly rendered apparent by touching it with a rod of glass or of wood.

* CADMIUM may be sublimed from some of its alloys, and is recognised by several of its properties, especially because, when heated in contact with the air, it is converted into brownish-yellow oxyde of cadmium (page 522).

* TELLURIUM is more difficultly volatilisable; heated in a small glass flask a bright-red heat is required to sublime it, and it condenses on the cold sides of the tube or flask in the form of small metallic drops, which resemble those of mercury, except that they are solid.

* VOLATILE SOLID ACIDS AND OXYDES.—The following belong to this class: OXYDE OF ANTIMONY, which first fuses into a yellow liquid, and then sublimes under the form of shining crystalline needles; TELLURIOUS ACID, which behaves nearly like the above, but is much more difficultly volatilisable, and which yields a sublimate, but which is not crystalline[1] (page 227); ARSENIOUS ACID, which is very easily sublimed; ARSENIC ACID, which is converted by a strong heat into oxygen gas and arsenious acid, and then yields the same sublimate as arsenious acid[2]; OSMIC ACID, which, being heated, sublimes in the form

of small white drops, with disengagement of a strong, pungent odour (page 329).

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[1] Berzelius says that, when operating on small quantities, tellurious acid is generally sublimed in the form of a powder; but sometimes also, though very rarely, the sublimate is in the form of crystals.—ED.

[2] Arsenious acid sublimes in the form of a white powder, which being softened

* VOLATILE SALTS.—The AMMONIACAL SALTS belong to this class, most of which are completely volatilised, or which sublime only partially when they contain a fixed acid (page 21). The ammoniacal salts may easily be distinguished from other salts by mixing them with soda, adding water to the mixture so as to form a pasty mass, and exposing it to a gentle heat upon a piece of platinum foil, by which means a strong odour of ammonia is evolved.

* Among the haloïd salts we must particularly mention the PERCHLORIDE OF MERCURY (corrosive sublimate), which begins to melt at a very gentle heat, and then sublimes; the SUBCHLORIDE OF MERCURY (calomel), which sublimes without previous fusion, and thus yields a sublimate which has a yellowish tinge whilst hot, but is white after perfect cooling. The two chlorides of mercury, like all the combinations of this metal, generally yield a sublimate of mercurial globules when mixed with soda, and then heated in a small glass flask or tube. The compounds of BROMINE and of IODINE with MERCURY behave nearly like the chlorides of that metal, except that *iodide of mercury*, which is red, yields a yellow sublimate, which, however, becomes red by trituration.

* Although we may not discover any volatile principles in a substance which we intend to analyse, yet it is frequently necessary to heat it in a small glass tube or flask in the flame of a spirit-lamp, when it strongly decrepitates, because this decrepitation might subsequently interfere with the operations to which this substance may ulteriorly be subjected. The substances which thus strongly decrepitate are generally *anhydrous salts*, and likewise many minerals found in nature, and amongst them certain metallic sulphurets and their compounds.

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by a more moderate heat acquires a vitreous texture; according to Berzelius, it is only when sublimed slowly and in capacious vessels that arsenious acid condenses into octahedral crystals. This white sublimate of arsenious acid has, however, a crystalline appearance when viewed through a magnifying glass.—ED.

* In some cases, after having thus heated the substance in question, it is to be treated with several re-agents, without removing it from the small glass tube or flask. This is done, as may be guessed from the preceding details, when it is suspected that it contains a combination of mercury. It is then to be mixed with an excess of well dried soda, heated first in the flame of the spirit-lamp, and the heat is subsequently increased by urging the flame with the blow-pipe. If the substance contain a combination of mercury, a grey coating of sublimed mercury will be formed. It sometimes happens that this grey coating cannot be immediately recognised as metallic mercury, in which case the operator is obliged to agglomerate the particles a little by touching it with a glass or a wooden rod, which renders the globules of mercury easily visible. If the substance contained water, or if the soda employed was not well dried, water is volatilised at the same time, which condenses in small drops on the cold sides of the tube, and which, subsequently flowing in the form of large drops, may break the tube; it is therefore advisable to heat the soda in a small crucible immediately before the experiment, in order to expel the water it might contain; it is likewise advisable to hold the tube as horizontally as possible. If the substance in question is a very volatile combination of mercury, for example, a combination of mercury with chlorine or with bromine, it may happen, especially if the heat be unskilfully managed, that the greatest part or almost the whole of that substance will volatilise before the soda has had time to decompose it, so that little or no sublimate of mercury is obtained; in such cases it is better that the soda employed be not altogether free from water, and not to heat the mixture in the flask or tube slowly, but on the contrary, to apply suddenly, if possible, a strong heat; but even then a portion of the combination is sublimed without having been decomposed. This inconvenience can be obviated only by moistening the mixture in the small flask or tube with water, and leaving it at rest for a few minutes before applying heat; but by acting

in this manner it is very difficult to avoid the breaking of the vessel whilst heating it.

* The only other re-agent besides *soda* which is resorted to in these experiments is *bisulphate of potash.* It is used for the purpose of recognising the acids contained in the salts after they have been separated from their bases by fusing these salts with this re-agent. It is employed especially for the purpose of ascertaining the presence of nitric acid in all NITRATES. The nitrates are to be mixed with some *bisulphate of potash,* and the mixture being introduced in a small glass flask or tube is to be heated in the flame of a spirit-lamp, without the help of the blow-pipe, by which means a disengagement of thick red fumes of nitrous acid is produced. The same process is employed to expel hydrofluoric acid from the COMBINATIONS OF FLUORINE, the presence of which is detected because it corrodes the neck of the flask or the inside of the tube. The COMBINATIONS OF IODINE heated in the same manner with *bisulphate of potash* yield violet fumes of iodine, and a black sublimate of iodine condenses on the cold sides of the tube, sulphurous acid being at the same time disengaged. The COMBINATIONS OF BROMINE treated in the same manner exhale also gaseous bromine, but generally in such small quantity that it does not constitute a conclusive test of the presence of bromine in such compounds.

* In order to detect the presence of SULPHURIC ACID in sulphates having a metallic oxyde for a base, the salt must first be deprived of the water which it may contain; it is then to be mixed with pulverised charcoal, and the mixture, being introduced in a small glass flask or tube, is to be heated by the blow-pipe, by which means a strong odour of sulphurous acid will be evolved.

SECOND OPERATION.

* AFTER having treated the substance under examination in a small glass flask or tube closed at one end, as mentioned in the

first operation, it is to be heated in a glass tube open at both ends [and held in an inclined position], first in the flame of the spirit-lamp alone, and then in the same flame urged by the blast of the blow-pipe. The object of this operation is to ascertain whether the substance being thus heated in a current of atmospheric air will yield any volatile matter. During this treatment the operator may increase or diminish the current of air through the tube, for if it be held in quite a horizontal position, the current of air is almost null; but it becomes more and more active as the tube is held more and more vertically.

* The volatile bodies which are produced whilst roasting the substance under examination in a current of atmospheric air, escape at times in the form of gases, which their odour may serve to recognise; at other times in the form of a sublimate, which condenses on the cold sides of the tube, and at a more or less considerable distance from the ignited substance, according to the greater or less degree of volatility.

A. GASEOUS SUBSTANCES, WHICH MAY BE RECOGNISED BY THEIR PECULIAR ODOUR DURING ROASTING.

* **Sulphurous acid** belongs to this order, and it is formed when the substance contains **metallic sulphurets**. The least quantity of this acid may be identified by its odour, when after having brought to a red heat the substance contained in the tube, held horizontally, the extremity of the tube is immediately brought under the nose whilst holding it as perpendicularly as possible. A strip of moistened brazil-wood paper introduced in the interior of the raised end of the tube is decolorised by the sulphurous acid. Almost all *metallic sulphurets* being thus treated disengage sulphurous acid. Some of them yield a sublimate of sulphur besides. This is the case especially with those which, when heated in the small glass flask, have already lost a portion of sulphur; yet this phenomenon depends also on the greater or less degree of inclination given to the tube whilst the roasting is taking place. Some *metallic sulphurets* yield

other sublimates besides, of which we shall speak further on. The native *sulphurets of zinc* and of *molybdenum* are those which yield *sulphurous acid* with most difficulty whilst roasting. When compounds of metallic sulphurets and arseniurets have been treated in a small glass flask, and have thus yielded a sublimate of arsenic, they may still exhale an odour of sulphurous acid when heated in a glass tube open at both ends; this is particularly the case with the arsenical pyrites.

* The presence of SELENIUM and of METALLIC SELENIURETS may likewise be recognised by the odour which is disengaged during the roasting; but no sublimate of selenium is obtained, especially when the tube is not held too horizontally.

* A few METALLIC ARSENIURETS exhale an odour of ARSENIC when roasted in the tube. This phenomenon, however, is produced only by those which, besides a sublimate of arsenious acid, yield one of arsenic also when the tube is not held too horizontally. If, whilst roasting the *metallic arseniurets* in the tube, nothing but arsenious acid is formed, no odour of arsenic is exhaled.

B. SUBSTANCES WHICH, BEING ROASTED IN A GLASS TUBE OPEN AT BOTH ENDS, YIELD A SUBLIMATE.

* IF the sublimate be *white*, it consists generally of oxydes, which sometimes exist ready formed in the substance under examination, and sometimes are formed by the oxydisation of the metal during the roasting. The following belong to this class:—

ARSENIOUS ACID.—This acid is formed during the roasting of *metallic arseniurets*, and condenses on the cold sides of the tube, in the form of a white sublimate, which has a crystalline appearance when viewed through a magnifying-glass. The smallest particle of this sublimed acid may then be treated as formerly indicated (page 344), for the purpose of determining whether it contains arsenic. Certain metallic arseniurets being roasted, yield arsenious acid more easily than other metallic arseniurets, and its production often requires that the substance be held for a long time at a red heat, by directing upon it the flame of the blow-pipe; such, for example, is the case with *grey cobalt*. Certain *metallic arseniurets* being roasted in a tube open at both ends, yield both *arsenious acid* and *metallic arsenic*. Submitted to the same treatment, the sulphurets of arsenic, or the substances which contain them, generally yield both *arsenious acid* and a *sublimate of red sulphuret of arsenic*, or even of *yellow sulphuret of arsenic*; the latter, as we have already observed[1], may be mistaken for sulphur. *Arsenious acid* may likewise be disengaged by roasting in a tube open at both ends, from substances which contain a great excess of *arsenious* or of *arsenic acids*, or which are principally composed of both these acids.

* OXYDE OF ANTIMONY.—This oxyde is sublimed when *antimony* or *metallic antimoniurets*, *sulphuret of antimony*, or combinations containing *sulphuret of antimony* are roasted, and likewise when *oxyde of antimony* or compounds containing it are heated in a tube open at both ends. The sublimate thus produced is white; a gentle heat is sufficient to shift it from one place to another, which circumstance chiefly characterises it (page 184). In most cases, however, the fumes produced in the tube by roasting substances which contain antimony are not due to *oxyde of antimony* alone, but to some *antimonious acid*, which is not volatile, it is true, but which, when the roasting takes place in contact with the air, is formed at the expense of the oxyde of antimony during its volatilisation, and condenses also in the cold sides of the tube under the form of a sublimate, above the point occupied by the substance under examination. Such a sublimate, consisting of oxyde of antimony and of antimonious acid, cannot therefore be wholly volatilised by heat. This sublimate is especially produced by the roasting of sulphuret of antimony, or of substances containing sulphuret of antimony, and of some metallic antimoniurets, principally when the metals combined with the antimony

are easily oxydisable. When the substances which contain *sulphuret of antimony* contain *lead* also (as, for example, in the mineral called *bournonite*), the roasting in the glass tube yields a white precipitate, which is partly volatile and partly non-volatile, and which consists of oxyde of antimony and of antimoniate of lead.

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[1] See page 594 and note.—ED.

* TELLURIOUS ACID.—The sublimate of *tellurious acid* is formed whilst roasting *tellurious acid* and *metallic tellurets*, also when *tellurious acid* and some of its combinations are heated in an open glass tube. The volatilised tellurious acid forms a white smoke, but is much less volatile than oxyde of antimony, from which it can therefore be easily distinguished, because it cannot be shifted from one place to another by heating it, and because the application of heat fuses it into colourless drops (page 230). When *metallic tellurets* contain *lead*, a sublimate of tellurious acid is formed, it is true, at a certain distance from the substance under examination, but another sublimate takes place nearer that substance, which is a combination of tellurious acid and oxyde of lead, which cannot be fused into drops, and which therefore might be mistaken for antimonious acid.

* CHLORIDE OF LEAD volatilises nearly in the same manner as tellurious acid, and fuses likewise into drops when heated.

* OXYDE OF BISMUTH is formed during the oxydisation (in the tube) of *sulphuret of bismuth*, and of the *alloys of bismuth with other metals*, but scarcely any sublimate is produced by roasting *bismuth itself*. The sublimate, being heated, fuses into drops, but which are brownish or yellowish, a character which distinguishes it from the sublimate of tellurious acid. A substance which contains bismuth, upon being heated red hot in the tube, becomes surrounded by a sublimate of fused oxyde of bismuth, which is of a dark-yellow colour whilst hot, but which becomes of a lighter hue in cooling. This phenomenon easily distinguishes bismuth from several other metals; but it is more difficult to distinguish it in this manner from LEAD, the combinations of which, when treated in that way, become likewise

surrounded with a fused yellow oxyde, the colour of which, however, is, after cooling, lighter than that of fused oxyde of bismuth. But we shall describe further on how these two metals may easily be distinguished from each other in their combinations.

* Other metals, besides *arsenic, tellurium, antimony,* and *bismuth,* yield a white sublimate when their combinations are heated in the open tube. Among these metallic compounds we may name SULPHURET OF LEAD and SELENIURET OF LEAD, which yield white sublimates of sulphate and of selenite of lead. These sublimates become grey when heated, and may thus be fused. (I have had already several times occasion to remark, that the combinations of lead with the metals and other substances, being heated in the tube, yield sublimates, when the effect of the oxydisation of these metals is to produce volatile metallic oxydes or acids.) PERSULPHURET OF TIN yields a thick smoke of peroxyde of tin, which cannot be volatilised by heat; MOLYBDIC ACID, heated in the open tube, is volatilised partly under the form of a white pulverulent sublimate, and partly under the form of brilliant crystals, with a slight yellowish tinge, whilst *sulphuret of molybdenum,* being treated in the same manner, yields sulphurous acid only, and no sublimate.

* All the sublimates which are formed by oxydising substances in the open tube are white, but the coloured substances which can be already volatilised out of the contact of the air in the small glass flask, are still more easily volatilised in the open tube. Most of the COMBINATIONS OF MERCURY yield a sublimate of metallic mercury when heated in the open tube; if *sulphuret of mercury* be thus treated, part of it volatilises without decomposition, and another portion yields likewise metallic mercury, which being more volatile than the sulphuret, condenses on the cold sides of the tube at a greater distance from the heated point. The CHLORIDES OF MERCURY are volatilised in the open tube without decomposition.

* I have indicated (page 440) how the METALLIC FLUORIDES

can be recognised by heating them in an open tube, with or without microcosmic salt.

THIRD OPERATION.

* AFTER having tried the substance in the small glass flask, and in the open tube, another portion is to be taken and heated by itself in the flame of the blow-pipe. The object of this operation is not only to ascertain whether the substance is fusible, but also to observe the change of colour which it undergoes, or which it communicates to the flame, and also the changes which it exhibits both in the oxydising and in the reducing flame. For this purpose the substance is heated according to the object in view, either on a charcoal support or between the platinum points of a forceps, or upon platinum wire.

* 1. In order to ascertain the degree of FUSIBILITY of substances before the blow-pipe, they are to be placed upon a charcoal support when they consist of metals, or of easily reducible metallic oxydes, or in general when they contain bodies susceptible of attacking platinum; and then they are exposed to the hottest part of the flame [that is to say, to the reducing flame]. If, however, the substance is composed of constituent principles which cannot attack platinum in the hot way, a small fragment or splinter of the substance is to be taken and exposed to the hottest part of the flame by holding it between the points of a platinum forceps. This latter process is especially applicable to substances which contain silicic acid, or other minerals which contain about the same principles, but in very different relative proportions, and which may very often be distinguished from each other by their different degrees of fusibility before the blow-pipe. If the substance under examination is in the form of small grains, one of them is to be placed upon the charcoal support, and the flame of the blow-pipe is directed upon it. If the substance be in powder, it may be kneaded with saliva, and a small portion is placed upon the

charcoal support; but in that case, if the substance be infusible, or difficultly fusible, the operator can hardly prevent its being carried away by the blast.

* Most METALS fuse before the flame of the blow-pipe, and all of them, except those called noble, are subsequently oxydised by the exterior flame. Among the noble metals, GOLD and SILVER fuse before the blow-pipe without undergoing the slightest change; PLATINUM, IRIDIUM, PALLADIUM, RHODIUM, OSMIUM, are infusible; yet *osmium* is converted, by the exterior flame, into osmic acid which volatilises. Among the other metals the oxydes of which are reducible by the interior flame, especially with the help of soda, MOLYBDENUM, TUNGSTEN, NICKEL, COBALT, and IRON, are infusible. Among the number of the metals which have not been named, there are several which are infusible also; but those cannot be obtained in the metallic state by means of the blow-pipe.

* Most METALLIC SULPHURETS fuse when treated before the blow-pipe upon charcoal, and this effect often takes place with sulphurets of metals, the oxydes of which are infusible; but many of these sulphurets become rapidly oxydised during the operation, and exhale an odour of sulphurous acid in the same way as when treated in the open tube, and are thus converted into metallic oxydes (page 475).

* Most of the pure METALLIC OXYDES are infusible; yet several of them, when treated in the exterior flame, pass to a higher degree of oxydisation; and when treated in the interior flame are reduced to a lower degree of oxydisation, or even to the metallic state. The infusible oxydes are—BARYTA and STRONTIA, the hydrates and carbonates of which are fusible, but are converted into the pure earths when heated upon charcoal, and then form infusible masses; LIME, which becomes very luminous when thus treated; MAGNESIA, ALUMINA, GLUCINA, YTTRIA, ZIRCONIA, which become very luminous also by the action of the heat; SILICIC ACID, TUNGSTIC ACID, OXYDE OF CHROMIUM, ANTIMONIOUS ACID, which, however, is reduced by

the interior flame into volatile oxyde of antimony; TANTALIC ACID, TITANIC ACID, PROTOXYDE OF URANIUM, PEROXYDE OF URANIUM, which is reduced by the flame of the blow-pipe to the state of protoxyde of uranium; PROTOXYDE OF CERIUM, which is converted by the blow-pipe into peroxyde of cerium; PEROXYDE OF CERIUM, SESQUIOXYDE OF MANGANESE, which parts with a portion of its oxygen when strongly heated; OXYDE OF ZINC, which is reduced by the interior flame, and thus becomes volatile; OXYDE OF CADMIUM, which is likewise reduced, and then volatilised by the interior flame; PEROXYDE OF IRON, which loses part of its oxygen in the interior flame; OXYDE OF NICKEL, OXYDE OF COBALT, PEROXYDE OF TIN, which may be reduced by the interior flame. The following small number of oxydes, on the contrary, are fusible when pure before the blow-pipe; they are—OXYDE OF ANTIMONY, which after fusion may be easily volatilised; OXYDE OF BISMUTH, PROTOXYDE OF LEAD, which like the preceding one may be reduced to the metallic state; and OXYDE OF COPPER.

* The degree of fusibility is a very important point to ascertain when the examination in question refers to the native COMBINATIONS OF SILICA and certain other MINERALS, for this characteristic feature displayed by the blow-pipe is often the only one by which we may distinguish those which consist of earths, and which contain no notable quantities of metallic oxydes, properly so called. In order to ascertain the degree of fusibility of minerals, the best way is to hold a fragment or splinter of the sample between the platinum points of a pair of forceps, and to expose it to the flame of the blow-pipe. Amongst the minerals most frequently met with, the following are infusible:—

Quartz,
Corundum,
Tourmaline, (both that which contains alumina, and even that which contains soda)
Spinell,
Pleonast,
Gahnite,
Olivine,
Cerite,

Zircon,
Cyanite,
Phenakite,
Leucite,
Talc,
Pyrophyllite,
Apatite,
Gehlenite,
Antophyllite,
Staurolite
Refractory clays,
Hydrate of alumina,
Hydrate of magnesia,
Sulphate of alumina,
Carbonate of lime,
Carbonate of magnesia,
Carbonate of zinc,
Allophane,
Cymophane,
Gadolinite (which being heated becomes suddenly luminous, as if it caught fire),
Vitreous tin,
Rutile,
Titanic iron,
Tantalite,
Turquoise,
Titaniferous oxyde of iron,
Chrome iron,
Native oxydes of iron,
Oxyde of uranium,
Tantalite,
Yttrotantalite,
Dioptase,
Chondrodite,
Topaz.

* Amongst those which are almost infusible and only become rounded at the edges, the following may be named :—

Felspar,
Albite,
Petalite,
Labradorite,
Anorthite,
Nepheline,
Tabular spar,
Pyroxène, (which contains much magnesia)
Meerschaum,
Soapstone, (*pierre de lard*)
Serpentine,
Mica, (some species, especially those found in agrnite)
Dichroite,
Epidote, (which intumesces by the first impression of the heat)
Emerald,
Euclase, (which intumesces by the first impression of the heat)
Titanite,
Sodalite,
Calcareous scheelin,
Heavy spar,
Celestine,
Gypsum,
Apatite,
Fluor spar.

* The following are fusible:—

Zeolites, (most of them intumesce)
Spodumene, (which intumesces)
Mejonite, (which froths up before fusing)
Eleolite,
Amphibole, (most of which boil up whilst in fusion)
Pyroxène, (those which contain no excess of magnesia)
Idocrase, (intumesces in fusing)
Garnet,
Cerine,
Orthite, (boils in fusing)
Ferruginous scheelin,
Boracite,
Hydroboracite,
Datolite,
Botryolite,
Cryolite,
Mica, (several species, especially those which contain lithia)
Tourmaline, (those which contain potash)
Axinite, (intumesces whilst fusing)
Amblygonite,
Lazulite,
Haüyne,
Nosian,
Eudialite,
Pyrosmalite.

* As to the SALTS which are soluble in water, most of them fuse when exposed to the flame of the blow-pipe upon a charcoal support, but they are then very often decomposed by the charcoal, upon which they leave their base, when it is of an infusible nature, in the pure state. The salts of alkalies after fusion are absorbed by the charcoal, or form beads.

* Among the insoluble salts several fuse into beads, which crystallise on cooling; this phenomenon is exhibited by PHOSPHATE OF LEAD more strongly than by any other salt, and it consequently can thereby be easily recognised (page 271).

2. THE CHANGES OF COLOUR WHICH SUBSTANCES UNDERGO BY THE ACTION OF HEAT, is generally owing to their being decomposed, and thus forming bodies of a different colour. There are some substances however, which, without undergoing any change in their composition, assume a colour different from that which they have at the ordinary temperature; they afterwards gradually lose the tinge which they have thus acquired, and after com-

plete cooling they reassume their original colour. Certain substances may therefore be thus accurately recognised, amongst which are the following:—

Oxyde of zinc, Titanic acid,	which are white at the ordinary temperature, and of a lemon-yellow colour at a higher temperature, which phenomena are likewise observable in a great number of other substances of a white colour, but in none so distinctly as in these two.
Peroxyde of lead, Suboxyde of mercury, Chromate of lead,	and a few other chromates, which at the ordinary temperature are yellow or red, but which become black at a higher temperature, though insufficient to decompose them.

* There are many substances, the ordinary colour of which becomes darker when they are heated; such are—

Protoxyde of lead,
Oxyde of bismuth.

* 3. THE COLOUR WHICH CERTAIN SUBSTANCES IMPART TO THE FLAME OF THE BLOW-PIPE may often be the means of distinguishing them. We have already shown (pages 7, 11, 16), the important value of this reaction for the purpose of indicating the presence of ALKALIES in salts. The flame of the blow-pipe exhibits likewise a change of colour when directed upon substances which contain STRONTIA (page 33), or LIME (page 37), and also upon PHOSPHATES moistened with sulphuric acid (page 271), and BORATES treated in the manner described (page 282). A colour is likewise imparted to the flame of the blow-pipe when employed to heat certain substances with re-agents.

* 4. THE DECOMPOSITIONS WHICH SOME SUBSTANCES EXPERIENCE BOTH IN THE EXTERIOR AND IN THE INTERIOR FLAME

consist principally in this, that they become oxydised in the exterior flame, whilst the oxydised bodies are reduced by treatment in the interior flame. The changes produced by the exterior flame generally resemble those which bodies undergo when heated in the glass tube open at both ends. It often happens, however, that substances are oxydised upon charcoal in the exterior flame, in order to be enabled to treat them more efficaciously afterwards by the appropriate re-agents. Thus, for example, metallic SULPHURETS and ARSENIURETS are roasted upon charcoal in the exterior flame, in order to separate the sulphur and the arsenic in the state of *sulphurous* and of *arsenious acids,* which decomposition or reaction is more readily effected with *sulphurets* than with *arseniurets.* The reduction of certain substances in the interior flame is generally effected in a better and more easy manner by mixing the substance with *soda,* and then heating it upon charcoal in the interior flame. The deportment of the various substances when so treated will be subsequently spoken of.

FOURTH OPERATION.

* AFTER having treated the substance under examination in the small flask, in the tube open at both ends, and having exposed them alone to the action of heat, they are next to be treated by the re-agents before the blow-pipe. The re-agents most in use in such experiments are SODA (carbonate of), MICROCOSMIC SALT, and BORAX. This operation is generally performed upon charcoal, though sometimes a *platinum* wire, or, in a very small number of cases, a *strip of platinum foil*[1] is used in preference.

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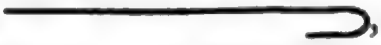
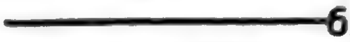
[1] The strip of platinum used may be about half an inch wide and about two inches long. It is very convenient for oxydising substances, in which case the flame of the blow-pipe should be made to play under the strips of platinum. Of course, no substance in the metallic form, nor such as are reducible into metal before the blow-pipe, should be treated upon the foil, because in such cases the reduced metal would combine with the platinum and perforate it; the platinum wire must be bent into a hook thus , or thus , and it is used by moistening it and plunging it in the substance, which will then adhere to it, (see Berzelius, vol. iv., page 13.—ED.

* 1. TREATMENT OF SUBSTANCES BY SODA.—Several substances, when treated with SODA upon CHARCOAL, fuse into a bead: this is a distinctive character. Other substances can be thus fused with *soda* only upon a PLATINUM WIRE: such is principally the case with the substances which play the part of an acid towards soda. Many oxydes being treated with soda in the interior flame are much more easily reduced than when treated *alone* in the same flame, and may be easily recognised. Lastly, there are several substances upon which soda has not the slightest action, which are not reduced by it upon charcoal, and which cannot be fused by it upon a platinum wire. These substances are principally the earths and a few metallic oxydes.

* A. Very few substances can BE FUSED INTO A BEAD WITH SODA UPON CHARCOAL. The only one which thus yields a colourless and limpid bead is SILICIC ACID, for which this circumstance constitutes a distinctive character[1], as we have already said (page 291). But besides pure silicic acid, the *silicates* which contain much of it may likewise be fused into a glass upon charcoal (page 291), because the silicate of soda is susceptible of dissolving part of the bases, which the soda has separated from the original silicates. The bead which is thus produced, however, is not always clear and transparent, but is coloured by several metallic oxydes. The fusion of the substance with soda into a bead is an important and distinctive feature for the native silicates. The following fuse with soda into a limpid bead:—

Quartz,
Feldspar,
Albite,
Petalite,
Spodumen,
Leucite,
Labradorite,
Meionite,
Anorthite,
Emerald,
Zeolytes, (in general)
Refractory clays,

* The following silicates can be fused with soda, but, generally,

the bead thus produced is coloured by the metallic oxyde of the substance:—

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[1] The fusion of silicic acid with soda is attended with an effervescence of carbonic acid.—ED.

Dioptase,
Achmite,
Lievrite,
Helvine,
Axinite,
Garnet, (several species)
Idocrase.

* Besides *silicic acid,* TITANIC ACID possesses also in an especial manner the property of fusing with soda upon charcoal; but the glass is opaque or greyish (page 299). The other substances either are not attacked by soda, and remain upon the charcoal into which the soda is absorbed, or else penetrate with the alkali into the charcoal, and are reduced.

* B. THE SUBSTANCES WHICH MAY BE FUSED WITH SODA UPON A PLATINUM WIRE IN THE EXTERIOR FLAME OF THE BLOW-PIPE ARE:—

Silicic acid,
Molybdic acid,
Tungstic acid,
Antimonious acid,
Chromic acid,
Tellurious acid,
Titanic acid,
The oxydes of manganese.

* The oxydes of manganese are, it is true, dissolved only in small proportion in the soda, but the smallest particle is sufficient to impart a green colour to this re-agent, by which means the presence of manganese can be easily recognised (page 66.) The colour is more distinct upon the foil than upon the wire of platinum. To the above number we must further add OXYDE OF COBALT (which likewise is soluble only in small quantity), OXYDE OF LEAD, and OXYDE OF COPPER[1].

* C. SUBSTANCES WHICH ARE REDUCED BY SODA UPON CHARCOAL IN THE INTERIOR FLAME.—Some of these oxydes are thus reduced into metal, which may be partially or totally volatilised by continuing to heat it in the interior flame, in which case the metal is re-oxydised during its volatilisation, and produces

a coating of oxyde upon the charcoal, which coating extends to a greater or less distance from the spot at which the substance mixed with soda is heated. Other reducible oxydes, the metal of which is not volatilisable, are reduced without producing any coating, as the above; the reduced metal may be subsequently obtained by pulverising the portion of the charcoal on which the reduction has been effected, and levigating it, after which the metal left behind may be easily recognised. It often happens, as we have already had occasion to remark, that oxydes are reduced into the metallic state upon charcoal, merely by the action of the interior flame of the blow-pipe; but in that case the reduction is effected more easily, and with more certainty, by adding soda to the oxyde. Most reducible oxydes require the help of soda for their reduction. Almost all the combinations of the reducible oxydes may likewise be reduced before the blow-pipe when mixed with soda,—an effect which is rarely obtained by the action of the blow-pipe alone, even though the oxyde contained in the combination is very easily reducible by it in the uncombined state. The combinations of the reducible metals with sulphur, selenium, chlorine, bromine, and iodine, are likewise reduced to the metallic state when treated with soda upon charcoal,—an effect which is not produced without soda, and by the flame of the blow-pipe alone; yet it is advisable in a great many cases to roast the metallic sulphurets and seleniurets upon charcoal in the exterior flame before reducing them with soda. The metallic arseniurets especially require to be carefully roasted, and thus deprived of their arsenic and oxydised before their metal can be reduced by soda. The use of soda is absolutely necessary when easily reducible oxydes have to be reduced from their combinations with inorganic acids. For example, in most cases it is not possible to reduce, without the use of soda, the metals from the sulphates, phosphates, arseniates, and other metallic salts, because the interior flame alone, instead of the pure metals, yields sulphurets, phosphurets, and arseniurets of these metals. Wherefore, the use of soda cannot be too strongly recommended to beginners, when the object is to reduce metallic oxydes combined with other substances.

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[1] *Oxyde of cobalt* fuses with soda into a pale-red mass, which is grey after cooling. *Oxyde of lead* forms a transparent glass which becomes opaque and yellowish on cooling. *Oxyde of copper* yields a fine green glass which partly loses its colour and becomes opaque in cooling.—ED.

* OXYDES AND COMBINATIONS OF OXYDES WHICH CAN BE REDUCED BY SODA UPON CHARCOAL IN THE INTERIOR FLAME OF THE BLOW-PIPE, BUT THE METALS OF WHICH ARE VOLATILE, AND ON THAT ACCOUNT DEPOSIT A COATING UPON THE CHARCOAL. To this class the following oxydes belong:—The OXYDES OF ANTIMONY: the reduced metal is brittle, it smokes much when it has been heated for a long time, and yields a white coating; TELLURIOUS ACID, which yields a white coating, and imparts a blue colour to the flame of the blow-pipe; OXYDE OF ZINC, which yields no metallic zinc, but only a coating which is of a yellowish colour so long as it is hot, but which is white after cooling: this coating is not altered by the exterior flame, but the interior flame causes it to disappear; OXYDE OF CADMIUM yields no metal, but a reddish-brown coating, the real colour of which can be well ascertained only after cooling; OXYDE OF BISMUTH, which may be easily reduced into metallic grains, which are brittle, and may be easily broken into pieces under the hammer: if the blowing be continued, a dark-yellow coating is formed upon the charcoal; OXYDE OF LEAD is likewise easily reduced into metallic grains, and by continuing to blow, the charcoal receives a yellow coating which resembles that of bismuth, but the reduced lead may be distinguished from bismuth, because the grains, instead of being brittle, may be flattened under the hammer.

* OXYDES AND COMBINATIONS OF OXYDES, WHICH CAN BE REDUCED BY SODA UPON CHARCOAL IN THE INTERIOR FLAME OF THE BLOW-PIPE, BUT THE METALS OF WHICH ARE NOT VOLATILE, AND CONSEQUENTLY DEPOSIT NO COATING UPON THE CHARCOAL.

* MOLYBDIC ACID, TUNGSTIC ACID, THE OXYDES OF IRON, OXYDE OF COBALT, OXYDE OF NICKEL, PEROXYDE OF TIN, OXYDE OF COPPER, OXYDE OF SILVER, and the oxydes of the metals called noble, which, however, are already reducible by the action of heat alone.

* When several reducible oxydes are contained in the substance to be analysed, alloys are often produced; sometimes also the reduced metals are obtained separately from each other. This is particularly the case when protoxyde of copper and peroxyde of iron are contained in one substance.

* The treatment by soda upon charcoal may also unequivocally detect the smallest traces of ARSENIC in the ARSENITES and ARSENIATES, which are thereby reduced into the metallic state, the smallest quantities of which may be recognised by the odour exhaled (pages 336, 343). It is possible also by the same process to detect SULPHUR in the METALLIC SULPHURETS, and in SULPHATES; SELENIUM in the metallic SELENIURETS, in the SELENIATES and SELENITES, not, however, with the help of soda alone, but by means of a glass of soda with silicic acid [glass of soda and silica] (pages 474, 204, 478, 221).

* D. SUBSTANCES WHICH ARE NOT ATTACKED BY SODA EITHER UPON A PLATINUM WIRE OR UPON CHARCOAL.—The substances belonging to this order are principally the following:—The OXYDES OF URANIUM and of CERIUM, TANTALIC ACID, ZIRCONIA, THORINA, YTTRIA, GLUCINA, ALUMINA, MAGNESIA, LIME, STRONTIA, BARYTA, and the ALKALIES. The *alkalies* are absorbed by the charcoal support on which they are heated. One may, with the help of soda, distinguish the *salts of alkalies* from those of the *earths*, by fusing them upon charcoal with this re-agent; the earthy salts remain in the charcoal, whilst those of the alkalies are absorbed by it.

II. TREATMENT OF SUBSTANCES BY MICROCOSMIC SALT.

* MICROCOSMIC salt is converted, by fusion before the blowpipe, into biphosphate of soda; the excess of acid of which dissolves almost all substances. SILICIC ACID is almost the only body which is insoluble therein by fusion, or at least it dissolves in it only in very minute proportion,—a property which, as we have said (page 291), may easily distinguish it in all its combinations. PEROXYDE OF TIN is likewise almost insoluble in

microcosmic salt, and it is partly on this account that metallic tin is sometimes used to effect reductions.

* It is ordinarily upon charcoal that substances are treated with microcosmic salt, more rarely upon a platinum wire, and they are subjected to the action both of the interior and of the exterior flame. In many cases the two flames produce different phenomena, especially when the metallic oxydes are such as to be easily convertible into lower or higher degrees of oxydisement. The effect of the exterior flame is to oxydise substances, and to make them pass from a lower to a higher degree of oxydisation; the interior flame, on the contrary, converts the higher degrees of oxydisation into lower ones, or reduces them to the metallic state. When substances are treated with microcosmic salt in the interior flame, and the operator ceases blowing, the globule should be very rapidly cooled; the best way of effecting this is to blow a current of cold air with the blow-pipe. When the cooling takes place gradually, it often happens that the substance re-oxydises a little. The reactions of the reducing flame by a prolonged blowing, may often be more easily produced by adding to the fused bead, whilst as yet hot, a very small piece of metallic tin, and re-heating the bead for a few moments. The oxydes which are difficultly reducible, and which cannot be converted into another degree of oxydisation, generally produce the same phenomena in both flames.

* Most oxydes yield, with microcosmic salt, colourless beads when they dissolve in this re-agent, but when a large quantity of microcosmic salt is employed, it very often happens that the bead is of an enamel-white colour after cooling. Many metallic oxydes, however, produce a coloured bead after fusion with microcosmic salt, which, especially for such oxydes, is an excellent re-agent. The colour of the bead is very often different in the exterior and in the interior flame. When a large quantity of such a substance has been dissolved in microcosmic salt, the colour of the bead is sometimes so deep that it cannot be well distinguished; when this is the case the bead must be flattened

by pressing it whilst hot, and before it has set hard, with one of the branches of the forceps[1].

* It is extremely difficult to give an accurate denomination to the colours of the beads tinged by a metallic oxyde. These colours often vary with the quantity of the substance held in solution, and very frequently also with the temperature of the bead, that is, whilst hot, and after complete cooling, added to which, certain colours have a different hue in day light, and in artificial light; such is the case, for example, with that which oxyde of cobalt imparts to the fluxes.

A. COLOURS IMPARTED TO A BEAD OF MICROCOSMIC SALT BY METALLIC OXYDES IN THE EXTERIOR FLAME.

* A COLOURLESS GLASS is produced by BARYTA, STRONTIA, LIME, MAGNESIA, GLUCINA, YTTRIA, THORINA, ZIRCONIA, all of which, however, when used in too large quantity give a milky tinge to the glass after cooling; by ALUMINA and MOLYBDIC ACID, the bead produced by these two substances has a slight tinge of green, and is colourless only when it has been melted upon a platinum wire, and after cooling; by TUNGSTIC ACID, and ANTIMONIOUS ACID, which, however, produce a glass slightly inclining to yellow; by TELLURIOUS, TANTALIC, and TITANIC ACIDS, OXYDE OF ZINC, OXYDE OF CADMIUM, and PEROXYDE OF LEAD: these three oxydes, when put in too large quantity, yield after cooling beads of a milky-white colour; lastly, by PEROXYDE OF TIN, which, however, is only very sparingly soluble in this flux.

* GREEN GLASSES are produced by OXYDE OF CHROMIUM, OXYDE OF URANIUM, and PROTOXYDE OF COPPER.

* YELLOW GLASSES, by OXYDE OF SILVER, OXYDE OF BISMUTH (the glass produced by the latter is almost colourless after cooling), and by VANADOUS ACID.

* RED GLASSES, by OXYDE OF CERIUM, PEROXYDE OF IRON,

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[1] The same object may be attained by drawing it out whilst soft into a thread, in which the colour may be distinctly perceived.—ED.

OXYDE OF NICKEL; but the intensity of the colour diminishes very much after cooling.

* BLUE GLASSES, by OXYDE OF COBALT.

* VIOLET GLASSES, by OXYDE OF MANGANESE.

B. COLOURS IMPARTED TO A BEAD OF MICROCOSMIC SALT BY METALLIC OXYDES IN THE INTERIOR FLAME.

* COLOURLESS GLASSES are produced by BARYTA, STRONTIA, LIME, MAGNESIA, GLUCINA, YTTRIA, THORINA, ZIRCONIA, ALUMINA, TANTALIC ACID, OXYDE OF ZINC, OXYDE OF CADMIUM, PEROXYDE OF TIN (all of which yield the same glass in the exterior flame), OXYDE OF CERIUM, OXYDE OF MANGANESE.

* GREEN GLASSES, by MOLYBDIC ACID, OXYDE OF CHROMIUM, VANADOUS ACID, OXYDE OF URANIUM, and PEROXYDE OF IRON.

* RED GLASSES, by FERRIFERROUS TUNGSTIC ACID, FERRIFERROUS ANTIMONIOUS ACID, FERRIFERROUS TITANIC ACID, and OXYDE OF NICKEL: the latter furnishes a glass, the colour of which becomes fainter on cooling.

* BROWN or REDDISH-BROWN GLASSES, by PROTOXYDE OF COPPER.

* BLUE GLASSES, by TUNGSTIC ACID and OXYDE OF COBALT.

* VIOLET GLASSES, by TITANIC ACID.

* GREY GLASSES, by TELLURIOUS ACID, OXYDE OF BISMUTH, OXYDE OF LEAD, and OXYDE OF SILVER, which colour is produced by the reduction of the metal.

III. TREATMENT OF SUBSTANCES BY BORAX.

* ALMOST all substances are dissolved by fusion with BORAX; some substances, however, are more soluble than others in this re-agent. Substances are best treated by *borax* upon a platinum wire, especially in order to judge well of the colour of the bead, because upon charcoal it is impossible to obtain a well-formed bead in so short a time as with microcosmic salt, because borax spreads at first upon charcoal, and requires a prolonged fusion to produce a bead with the substance under examination. The metallic oxydes generally dissolve well in *borax*, and with the

same colour as in microcosmic salt; there are, however, some exceptions, but which on that account are characteristic. When substances are treated by *borax*, the exterior and the interior flame produce the same differences as with microcosmic salt. The solution of some substances in borax yields glasses which are limpid, both before and after cooling, even when they contain a large quantity of these substances; but by directing the exterior flame upon them in an unequal and intermittent manner, they become opaque and similar to enamels. This is a characteristic phenomenon for some substances, and it takes place much more rarely when these same substances are treated by microcosmic salt. Most of the oxydes yield a colourless glass with borax, just as with microcosmic salt.

A. COLOURS IMPARTED TO A BEAD OF BORAX BY METALLIC OXYDES IN THE EXTERIOR FLAME OF THE BLOW-PIPE.

* Colourless glasses are produced by baryta, strontia, lime, magnesia, glucina, yttria, zirconia, tantalic acid, titanic acid, oxyde of zinc, oxyde of cadmium, oxyde of silver (the solutions of which in borax, when they contain much oxyde, become turbid, "*au flamber*"[1]), alumina, thorina, silicic acid, tellurious acid, oxyde of bismuth, antimonious acid, tungstic acid, molybdic acid, and peroxyde of tin, which is only slightly soluble in borax.

* Green glasses, by oxyde of chromium and protoxyde of copper.

* Yellow glasses, by vanadous acid, oxyde of uranium, and oxyde of lead, which becomes almost colourless on cooling.

* Red glasses, by oxyde of cerium (the glass of which may be rendered turbid, "*au flamber*"[1]), peroxyde of iron, and oxyde of nickel, the colour of all of which becomes lighter, or even vanishes on cooling.

* Blue glass, by oxyde of cobalt.

* Violet glass, by oxyde of manganese.

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[1] "Flamber" means directing the exterior flame of the blow-pipe upon the substance in an irregular or intermittent manner.—Ed.

B. COLOURS IMPARTED TO A BEAD OF BORAX BY METALLIC OXYDES IN THE INTERIOR FLAME OF THE BLOW-PIPE.

* Colourless glasses are produced by **baryta, strontia, lime, magnesia, glucina, yttria, zirconia, tantalic acid, oxyde of zinc, oxyde of cadmium, alumina, thorina, silicic acid, peroxyde of tin** (all of which yield a like glass in the exterior flame), **oxyde of cerium**, and **oxyde of manganese.**

* Green glasses, by **oxyde of chromium, vanadous acid, oxyde of uranium**, and **oxyde of iron.**

* Yellow glasses, by **tungstic acid.**

* Brown or reddish-brown glass, by **molybdic acid**, and **protoxyde of copper.**

* Blue glasses, by **oxyde of cobalt.**

* Violet glasses, by **titanic acid** (the bead may be rendered turbid, "*au flamber.*"[1])

* Grey glasses, by **antimonious acid, tellurious acid, oxyde of nickel, oxyde of bismuth**, and **oxyde of silver**: this colour is owing to a reduction of metal.

* From what has been said, it may be seen that the oxydes which form coloured beads with microcosmic salt, and with borax, cannot be confounded with each other, for there are no two oxydes which give the same colours with these two re-agents, and with the exterior and interior flame of the blow-pipe. When there are two, or even several of these oxydes in the substance under examination, their presence may be generally recognised by submitting it, with these two re-agents, microcosmic salt and borax, to the four operations of which we have been speaking.

There are only a small number of cases in which other re-agents are employed, besides those which have been mentioned, but they are resorted to only for the detection of certain substances. For example, BORACIC ACID and IRON WIRE, for the detection of *phosphoric acid* (page 270); solution of NITRATE OF COBALT, to detect *magnesia* (page42), *alumina* (page 47), and likewise *oxyde of zinc* (page 73); OXYDE OF NICKEL, to detect *potash* (page 5); PROTOXYDE OF COPPER, to detect the *combinations of chlorine, iodine* and *bromine* (pages 424, 435, 430); lastly, PULVERIZED FLUORSPAR, which is very convenient to distinguish *sulphate of baryta, sulphate of strontia,* and *sulphate of lime,* from other substances (pages 28, 33, 37 [1]).

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[1] See preceding note.—Ed.

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[1] Since the publishing of Berzelius's Treatise, another work by C. J. Plattner has appeared, ably translated into English by Dr. Muspratt, in which, especially those engaged in mining operations, will find indications for the determination of the metallic constituents of minerals, not only qualitatively but quantitatively also, at least approximatively.—ED.

CHAPTER V.

SYSTEMATIC COURSE OF QUALITATIVE ANALYSES OF COMPOUNDS WHICH ARE SOLUBLE IN WATER, AND WHICH CONSIST ONLY OF A BASE COMBINED WITH AN ACID, OR OF A METAL COMBINED WITH A NON-METALLIC BODY, THE CONSTITUENT PARTS BEING AMONG THE FOLLOWING SUBSTANCES:—

BASES.

1. Potash,
2. Soda,
3. Ammonia,
4. Baryta,
5. Strontia,
6. Lime,
7. Magnesia,
8. Alumina,
9. Protoxyde of manganese,
10. Oxyde of zinc,
11. Oxyde of cobalt,
12. Oxyde of nickel,
13. Protoxyde of iron,
14. Peroxyde of iron,
15. Oxyde of cadmium,
16. Oxyde of lead,
17. Oxyde of bismuth,
18. Protoxyde of copper,
19. Oxyde of silver,
20. Suboxyde of mercury,
21. Protoxyde of mercury, (peroxyde of mercury)
22. Oxyde of gold,
23. Protoxyde of tin,
24. Peroxyde of tin,
25. Oxyde of antimony.

ACIDS AND NON-METALLIC BODIES.

1. Sulphuric acid,
2. Nitric acid,
3. Phosphoric acid,
4. Arsenic acid,
5. Boracic acid,
6. Carbonic acid,

or

7. Chlorine,
8. Sulphur,

which in the substance under examination are combined with the metals of the bases enumerated above.

* The first operation in the qualitative analysis of a substance in the humid way is to examine whether it is completely or partially soluble or insoluble in water. It will be seen from the indications which I shall give for the analysis of the substances which are not soluble in water, that that of the bodies which are soluble in this menstruum is much more simple and easy.

* Whether the substance under examination is soluble or insoluble, may be easily ascertained, if the substance is sufficiently abundant, by taking a small quantity of it, about 1 gramme (about 15 or 20 grains), and agitating or stirring it in a test-tube or glass with distilled water[1]. If the substance is not thus completely dissolved, heat is applied to the whole by means of a small spirit-lamp. If the substance cannot be completely dissolved, a small portion of the water with which it has been stirred must be filtered, and a few drops being placed upon a strip of platinum foil are to be carefully evaporated thereon with the flame of the spirit-lamp. If an abundant residuum be left on the platinum, it is a proof that the substance is partially soluble in water; if no residue is left on the platinum foil it is a proof that the substance is totally insoluble in water.

* Sometimes a slight residue is left on the platinum foil. This is a proof that the substance contained a constituent principle difficultly soluble, though not completely insoluble, in water, as for example, SULPHATE OF LIME; or else this substance is insoluble in water, but the water employed was not pure.

* This last circumstance,—I mean the want of perfect purity of the re-agents employed,—is frequently a cause of error for those who have not yet acquired the habit of qualitative analysis, for it is only experience that teaches how to distinguish in a substance the principles which are essential from those which are only in the state of accidental mixture.

* He who wishes to engage in chemical analysis with a view to his personal instruction, should first choose substances, the

composition of which he knows to be simple, and undertake those of a complex nature only afterwards. I have by long experience become convinced that it is the best method. Beginners will find no difficulty in procuring substances consisting of only few elements, yet the composition of which is unknown to them.

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[1] About 10 or 12 times its bulk of distilled water will answer the purpose.—Ed.

* I purpose in the present chapter, and the two following, to indicate a systematic course for the detection of the constituent principles of compounds which consist of only one base and one acid, or of a metal with a non-metallic body, taking care to avoid including those which are rare. And as we have said that it is more easy to detect the component parts of the substances which are soluble in water, we shall suppose in these three chapters that the substance which it is intended to analyse is susceptible of dissolving in water.

* In looking over the list of the bases and acids at the beginning of this chapter, it will be readily perceived by those who have some knowledge of chemistry, that all these bases cannot be found combined with all these acids in soluble compounds, nor all the metals of these oxydes with all the non-metallic bodies.

* The following bases form, with SULPHURIC ACID, compounds which are insoluble, or at any rate very sparingly soluble, and which consequently cannot be found amongst the substances under present consideration:—*baryta, strontia, lime, oxyde of lead,* and even *suboxyde of mercury*. The combinations of *sulphuric acid* with *oxyde of bismuth, peroxyde of mercury,* and *oxyde of antimony,* are decomposed by water, which precipitates them in the state of a basic salt, whilst an acid salt remains in solution. The combination of *sulphuric acid* with *oxyde of gold* is unknown. The other bases form, with sulphuric acid, compounds which are soluble at least in the neutral state, for some of those which are basic may be insoluble; several of them, for example, *sulphate of silver,* without being very soluble, are nevertheless sufficiently so not to be classed amongst the salts difficultly soluble.

* Almost all the bases mentioned in the list yield, with NITRIC ACID, compounds which are soluble, at least in the

neutral state, for a few *basic nitrates* are insoluble, or sparingly soluble. The *peroxyde of tin* and *oxyde of antimony* are not soluble in this acid. Water decomposes its combinations with *oxyde of bismuth, peroxyde* and *suboxyde of mercury.* Its combinations with *oxyde of gold* are unknown.

* PHOSPHORIC and ARSENIC ACIDS hardly form soluble compounds with any other substances but the alkalies. Those with the earths and the *metallic oxydes* are insoluble, at least in the neutral and in the basic state, and cannot be dissolved except in the free acids.

* The combinations of BORACIC ACID with the *alkalies* are soluble, but those with the *earths,* or the *metallic oxydes,* are mostly very sparingly soluble, though, properly speaking, not quite insoluble.

* CARBONIC ACID likewise forms soluble compounds with the *alkalies* only; those with the *earths* and *metallic oxydes* are insoluble.

* CHLORINE forms insoluble compounds with the greatest part of the metals in the list. *Chloride of silver* and *subchloride of mercury* are insoluble; *chloride of lead* is sparingly soluble. The oxydes of these three metals cannot therefore be found dissolved in water in presence of muriatic acid. *Chloride of bismuth, protochloride of tin,* and *chloride of antimony,* are decomposed by water, and in order to re-dissolve the precipitate, muriatic acid must be added.

SULPHUR forms compounds which are soluble in water only with the metals of the *alkalies* and of the *alkaline earths;* several of the latter are sparingly soluble. The metallic sulphurets, properly so called, are insoluble.

1. COURSE OF THE ANALYSIS TO DETECT THE BASE.

A. A portion of the aqueous solution of the substance under examination is to be concentrated and then rendered slightly acid. This is best effected by adding a few drops of muriatic acid; very dilute nitric acid is to be used only if *oxyde of silver, suboxyde of mercury,* or a great quantity of *protoxyde of lead* be present, which may be known when the addition of a few drops of muriatic acid to a portion of the liquor produces a white precipitate[1]. To this acidulated solution, enough sulphuretted hydrogen water strongly saturated is added to make it smell distinctly of sulphuretted hydrogen[2]; if no precipitate is thereby produced, the base is one of those from No. 1 to 13. If, on the contrary, a precipitate is formed, the base is one of those from No. 13 to 25, and is therefore either **PEROXYDE OF IRON, OXYDE OF CADMIUM, PROTOXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, PROTOXYDE OF MERCURY, OXYDE OF GOLD, PROTOXYDE OF TIN, PEROXYDE OF TIN,** or **OXYDE OF ANTIMONY**[3].

If the precipitate produced [in the acidified liquid] by sulphuretted hydrogen water is *black*[4], then the base is from No. 16 to 22, and is consequently either **PROTOXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, PROTOXYDE OF MERCURY,** or **OXYDE OF GOLD.** These oxydes may be distinguished from each other in the following manner:—

To a small portion of the dissolved compound, ammonia is to be added; if it then assumes a deep blue colour, and if an excess of ammonia produces no precipitate, the base is **PROTOXYDE OF COPPER.**

A portion of the very concentrated solution of the compound acidified with muriatic acid is to be diluted with water. If a milkiness and a white precipitate be thus produced which remains insoluble in a large quantity of water, the base is OXYDE OF BISMUTH[1].

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[1] The white precipitate produced by the addition of muriatic acid is of course a *chloride* of the metal of one of the three oxydes alluded to, and they may at once be summarily identified in the following manner, namely:—If an addition of an excess of ammonia re-dissolves the precipitate, it is *silver;* if the precipitate, instead of being thus dissolved by ammonia, merely turns black, it is *suboxyde of mercury;* but if the precipitate remains unchanged by the addition of ammonia, the precipitate is *lead,* and then the addition of a large quantity of boiling water should dissolve it. In order, however, to remove all doubts as to the real existence of the above metals, they should further be tested as mentioned in the first part of this work, and as will presently appear.—ED.

[2] Instead of sulphuretted hydrogen water, a current of sulphuretted hydrogen gas may be passed for a while through the acidified liquid.—ED.

[3] These oxydes, as precipitated by sulphuretted hydrogen, are of course in the state of sulphurets of the metals.—ED.

[4] The precipitate, instead of being *black,* is sometimes *brownish-black,* especially if only a trace of these substances exists in the solution.—ED.

To a portion of the solution, add one or a few drops of muriatic acid. If a white precipitate be thus formed which does not disappear by the addition of a large quantity of water, the base is either OXYDE OF SILVER or SUBOXYDE OF MERCURY, which may be distinguished from each other as follows:—

To a portion of the solution of the compound, one drop, or at most a few drops, of ammonia are to be added. If a deep black precipitate is thus produced, insoluble in an excess of ammonia, but merely rendered less intensely black thereby, or if the solution being very acid, this addition of ammonia determines a grey precipitate insoluble in an excess of the re-agent, the base is SUBOXYDE OF MERCURY.

When, on the contrary, one or at most a few drops of *ammonia* produce in the solution a brown precipitate, which immediately disappears by the addition of a larger quantity of volatile alkali; or if the addition of ammonia produces no precipitate in the solution, especially if it be acid, the base is OXYDE OF SILVER.

To a portion of the solution an excess of solution of *potash* is added. If this produces a *yellow* precipitate, the base is PROTOXYDE OF MERCURY[2].

To a portion of the original solution, one of *protosulphate of iron* is added. If a brown precipitate be thereby produced, which after settling has all the qualities of metallic gold, the base is OXYDE OF GOLD[3].

To the original solution a little dilute *sulphuric acid*, or some solution of a *sulphate* is added. If a white precipitate [of sulphate of lead] is the result, the base is PROTOXYDE OF LEAD.

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[1] When the acid solution of the compound contains only a small quantity of oxyde of bismuth, the precipitate produced therein by sulphuretted hydrogen is dark-brown. Bismuth can hardly exist in an aqueous solution without the presence of a free acid, or unless it be in the state of an acid salt.—ED.

[2] This yellow precipitate is hydrate of protoxyde of mercury. See page 136.—ED.

[3] If the quantity of gold in the solution be very small, the addition of protosulphate of iron produces only a blue colour, at least at first, for after a while a brown powder of metallic gold is deposited.—ED.

When the precipitate produced by the *sulphuretted hydrogen* water is milky white [of sulphur], the base is PEROXYDE OF IRON.

If the precipitate produced by *sulphuretted hydrogen* be yellow, the base is PEROXYDE OF TIN or OXYDE OF CADMIUM, which may be distinguished from each other as follows[1]:—

To a portion of the original solution, *hydrosulphuret of ammonia* is to be added; if this solution be acid, it should first be neutralised with ammonia, and if a yellow precipitate, insoluble in any excess of hydrosulphuret of ammonia, be produced, the base is OXYDE OF CADMIUM.

If, on the contrary, the addition of *hydrosulphuret of ammonia* to a portion of the original solution, previously neutralised by ammonia, if it be acid, produces a yellow precipitate easily soluble in an excess of hydrosulphuret of ammonia, the base is PEROXYDE OF TIN.

If the precipitate produced by the aqueous solution of *sulphuretted hydrogen* be dark-brown, the base is PROTOXYDE OF TIN.

If the precipitate produced by the aqueous solution of *sulphuretted hydrogen* be orange-red, the base is OXYDE OF ANTIMONY[2].

B.—When, after having acidified the solution of the substance under examination, the addition of *sulphuretted hydrogen* produces no precipitate, then the base is not one of those from No. 14 to No. 25[3]. The solution of the compound, if acid, is first to be neutralised with ammonia, and *hydrosulphuret of ammonia* is then to be added to it. If this re-agent produces a precipitate, the base is one of those from No. 8 to 13, and is not one of those from No. 1 to 7. It is, therefore, either ALUMINA, PROTOXYDE OF MANGANESE, OXYDE OF ZINC, OXYDE OF COBALT, OXYDE OF NICKEL, or PROTOXYDE OF IRON.

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[1] The yellow precipitate is not immediately produced in dilute, neutral, or acid solutions of peroxyde of tin, but only after a while or by boiling. The precipitate augments by standing.—ED.

[2] The solution must be decidedly acid; for if neutral, the addition of sulphuretted hydrogen would only at first impart a red colour to the solution without forming a precipitate. In such a case, however, the addition of muriatic acid either before or after, or the applying of heat, immediately determines the orange-red precipitate of sulphuret of antimony.—ED.

[3] The solution tested by sulphuretted hydrogen must always be decidedly acid, since several substances are precipitated from neutral or very slightly acid solutions by sulphuretted hydrogen; for example, *oxyde of zinc* is not precipitated from

If the precipitate produced by *hydrosulphuret of ammonia* is black, the base is one of those from No. 11 to 13; namely, OXYDE OF COBALT, OXYDE OF NICKEL, PROTOXYDE OF IRON: these three bases may be distinguished from each other as follows:—

To a portion of the original solution add some solution of *carbonate of potash* or *of soda*.

If the precipitate produced thereby be first white, then green, and ultimately reddish-brown at the surface, the base is PROTOXYDE OF IRON[1].

If the precipitate is dirty red, the base is OXYDE OF COBALT[2].

If the precipitate is bright green, the base is OXYDE OF NICKEL.

If the precipitate produced by *hydrosulphuret of ammonia* is of a flesh-colour, the base is PROTOXYDE OF MANGANESE.

If, on the contrary, the precipitate thus produced by hydrosulphuret of ammonia is white[3], the base of the compound is

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a distinctly acid solution, but if the solution be only neutral, sulphuretted hydrogen will cause a white precipitate. The operator must therefore make sure that the solution contains a strong acid in the free state, especially as the neutral solutions of the salts of zinc redden litmus paper.—ED.

[1] The black precipitate of sulphuret of iron produced by hydrosulphuret of ammonia being left in contact with the air absorbs oxygen and very soon becomes reddish-brown, which is already a distinctive character, because the black sulphuret of cobalt or of nickel produced by the same re-agent, is far from becoming oxydised so rapidly by exposure. By filtering this precipitate it almost immediately turns reddish-brown on the filter, because the points of contact with the air are of course much increased.—ED.

[2] This dirty red precipitate is a subcarbonate of cobalt, which becomes blue by boiling.—ED.

[3] The least trace of iron imparts a grey colour to the precipitate produced by hydrosulphuret of ammonia, and if the proportion of iron be larger, the precipitate is darker still, or black.—ED.

either OXYDE OF ZINC or ALUMINA, which two bases may be distinguished from each other as follows:—

To a portion of the original solution add ammonia. If the precipitate thereby produced is white, and soluble in an excess of this re-agent, the base of the salt is OXYDE OF ZINC.

If, on the contrary, the precipitate thereby produced is not dissolved by an excess of ammonia, the base is ALUMINA.

C.—If the acidified solution of the substance under examination affords no precipitate with the aqueous solution of sulphuretted hydrogen, nor the neutral solution with hydrosulphuret of ammonia, the base of the compound does not belong to those from No. 8 to 25, but is one of those from No. 1 to 7; consequently, it is either POTASH, SODA, BARYTA, STRONTIA, LIME, or MAGNESIA. To discriminate which of these substances is the base sought after, pour in a portion of the neutral solution[1] of the compound, some solution of carbonate of potash or of soda. If this produces a white precipitate the base is one of those from No. 4 to 7, and not one of those from No. 1 to 3.

To distinguish the four bases, from No. 4 to 7, namely, BARYTA, STRONTIA, LIME, MAGNESIA, some ammonia must be poured in the original solution rendered neutral. If a white, flocculent precipitate is produced thereby, the base is MAGNESIA. (We should remark, however, that if the solution instead of being neutral, is acid, ammonia will produce no precipitate, even though the base be magnesia)[2].

To distinguish the other three bases, BARYTA, STRONTIA and LIME, which are not precipitated by ammonia from a neutral solution, a concentrated solution of SULPHATE OF LIME is to be added to the concentrated solution of the compound. If a precipitate is immediately produced by it, the base is BARYTA. If the precipitate appears only after a time, the base is STRONTIA; if no precipitate is formed, the base is LIME[1].

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[1] If, whilst neutralising the solution by ammonia, a white precipitate is formed, it is a proof of the presence of magnesia. (See below.)—ED.

[2] This is owing to the formation of an ammoniacal salt, which, if the acid be in sufficient quantity, prevents the precipitation of the magnesia. We have seen, in fact, in the first part (page 40), that the presence of a salt of ammonia prevents the precipitation of magnesia, but that a precipitate of hydrate of magnesia produced in a neutral solution is dissolved by the addition of muriate or any other salt of ammonia. The best test for *magnesia* in an acid solution, or one which contains much ammoniacal salt, is phosphate of soda, which determines therein a white crystalline precipitate, especially by boiling (page 40).—ED.

In order to distinguish more conclusively still BARYTA from STRONTIA, *hydrofluosilicic acid* should be poured in the solution of the salt under examination. If after a time a precipitate is thereby produced, the base is BARYTA; if no precipitate appears, the base is STRONTIA[2].

D.—If the acidified solution of the substance under examination yields no precipitate by treatment with *sulphuretted hydrogen* water, nor the neutral solution by *hydrosulphuret of ammonia,* nor yet by *carbonate of potash* or *of soda,* the base does not belong to those from No. 4 to 25, but is one of those from No. 1 to 3, and is therefore either POTASH, SODA, or AMMONIA.

These three bases may be distinguished from each other in the following manner:—To a portion of the concentrated solution of the substance, add a concentrated solution of *potash;* if an odour of ammonia is disengaged, and further, if white clouds are produced by holding at the surface of the liquid a glass rod moistened with dilute muriatic acid, the base is AMMONIA.

If nothing of the kind is produced, some alcoholic solution of chloride of platinum is to be poured in the concentrated solution of the substance, and if a yellow precipitate is thereby produced, the base is POTASH.

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[1] This negative proof should, however, be confirmed by adding oxalic acid, or better still, a solution of oxalate of ammonia to that of the compound, which will determine a white precipitate of *oxalate of lime* if that base be present. The solution should be dilute. It should be borne in mind that if oxalic acid or an oxalate is present in the solution, the addition of solution of *sulphate of lime* will produce a white precipitate of oxalate of lime, which must not be mistaken for one of sulphate of baryta.—ED.

[2] The original solution must be acid, or at most neutral, for hydrofluosilicic acid when poured in a solution of ammonia produces an abundant precipitate of silicic acid, which would be the case if the solution under examination contained free ammonia.—ED.

If no precipitate is thereby formed, the base of the compound is SODA[1].

2. COURSE OF THE ANALYSIS TO DETECT THE ACID OR THE NON-METALLIC BODY.

A. To a portion of the solution of the compound, muriatic acid is to be added. If an effervescence takes place, the solution contains CARBONIC ACID or SULPHUR in combination with one of the metals of the bases in the list.

If the gas disengaged from the liquor with effervescence has the well-known odour of sulphuretted hydrogen, the solution contains a metallic sulphuret. If, on the contrary, the gas which escapes with effervescence is inodorous, the acid of the compound is CARBONIC ACID[2].

B. If muriatic acid produces no effervescence, the neutral solution must be diluted with a sufficient quantity of water, and solution of *chloride of barium* must be added. If a precipitate is thus produced, the liquor contains either SULPHURIC ACID, PHOSPHORIC ACID, ARSENIC ACID, or BORACIC ACID[3]. These substances may be distinguished from each other in the following manner:—

To the precipitate produced by *chloride of barium* in the neutral solution add a small quantity of a free acid, and in preference to any other, of *muriatic acid*. If the precipitate remains unaltered, the acid of the combination is SULPHURIC ACID. If, on the contrary, the free acid and an addition of water dissolves the precipitate, the compound contains either PHOSPHORIC ACID, ARSENIC ACID, or BORACIC ACID. These three substances may be distinguished as follows:—

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[1] This negative test should be rendered conclusive by antimoniate of potash (see the note page 14), and by the yellow colour of the blow-pipe, and of the flame of alcohol (page 13).—ED.

[2] The addition of muriatic acid poured in a solution of a carbonate sometimes fails in producing an effervescence. This happens when the quantity of the carbonate is small, or, which is the same, when its solution is dilute, and it is owing to this that the carbonic acid liberated dissolves in the water of the solution. Even though the quantity of carbonate be larger or even considerable, the addition of the acid may at first cause only a slight effervescence, or even no effervescence, because the carbonic acid liberated combines with a portion of the undecomposed carbonate, and converts it into a bicarbonate (see page 383).—ED.

[3] The presence of boracic acid in the solution may escape detection when tested by chloride of barium, if the solution is very dilute, or if it contain ammoniacal salts, at least in too great quantity; because, on the one hand, borate of baryta being slightly soluble in water would not in that case be precipitated; and, on the other, because the presence of ammoniacal salts prevents the precipitation of borate of baryta. Neither should too much chloride of barium be added, since borate of soda is soluble in an excess of this re-agent.—ED.

A portion of the compound reduced to powder is put in a platinum or porcelain crucible, or in a small porcelain dish, and moistened with a few drops of *sulphuric acid; alcohol* is then to be added, and set fire to. If the flame of the alcohol be green, the acid of the compound is BORACIC ACID[1].

If the compound contains no boracic acid, a portion of the solution of the compound should be acidified by an acid, but in preference by muriatic acid, and then, *sulphuretted hydrogen water* being added, the whole is to be heated. If, after some time, a yellow precipitate is formed, the acid of the compound is ARSENIC ACID[2].

If this reaction does not take place, and provided the operator has ascertained that no *boracic acid* is present, then the acid of the compound is PHOSPHORIC ACID[3].

C. If the experiments above related have demonstrated the absence of CARBONIC ACID, SULPHURIC ACID, BORACIC ACID, ARSENIC ACID, PHOSPHORIC ACID, and of SULPHUR, in the substance under examination; *nitrate of silver* must be added to a portion of the solution. If this produces a white precipitate insoluble in dilute nitric acid, the compound contains CHLORINE[1] in combination with one of the metals of the twenty-five bases in the list.

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[1] If the compound to be examined is in the state of solution, it must be evaporated; the mass obtained is then tested, as just said, with sulphuric acid and alcohol. Care must be taken in evaporating, because the boracic acid volatilises with the aqueous vapour.—ED.

[2] In testing for the bases this yellow precipitate may have been produced, and it may be confounded with oxyde of cadmium or with peroxyde of tin, which yield also a yellow precipitate when this acid solution is treated by sulphuretted hydrogen; but the yellow sulphuret of arsenic is distinguished from the yellow sulphuret of cadmium, because the first is soluble in hydrosulphuret of ammonia and in potash, whilst the second is insoluble therein; and it differs from the yellow persulphuret of tin, because the first is volatile at a high temperature, which is not the case with the second. But the most characteristic test is the blow-pipe and the other re-agents mentioned (page 331), which preclude the possibility of error. If the presence of arsenic acid is thus demonstrated, the base of the compound must have been found to be an alkali, since the alkaline arseniates only are soluble in water.—ED.

[3] This is, however, a negative proof which should be rendered positive and conclusive by testing with nitrate of silver, sulphate of magnesia with some free ammonia, and before the blow-pipe. Nitrate of silver is the best test, but the absence of arsenious acid must be previously ascertained. (See pages 262, 341).—ED.

D. When it has been ascertained that the compound contains no CARBONIC, SULPHURIC, BORACIC, ARSENIC, PHOSPHORIC ACIDS, nor SULPHUR, nor yet CHLORINE, a portion of the dry compound should be heated with a little charcoal powder. If the combustion of the charcoal is burning actively with a deflagrating noise, the acid of the compound is NITRIC ACID[2].

When by means of the above experiments the operator thinks that he has detected the base and the acid of the compound, it is absolutely necessary to resort to another series of experiments in order to acquire the conviction that the results obtained are accurate. With this view the base and the acid must be submitted to the greatest possible number of the tests enumerated in the first part of this volume, and those re-agents should be chosen in preference which produce the most characteristic reactions, and distinguish most clearly the substance under examination from other substances which it might resemble. I have always taken care to point out the re-agents which act in a characteristic manner. It is only after these further experiments that the analyst can rely upon the accuracy of the results obtained in the first instance. This rule is without exception, and applies to all cases of qualitative analysis. The beginner sometimes finds difficulties in following it when the substances operated upon, instead of being pure, are mixed with small quantities of other substances which may modify the action of the re-agents.

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[1] If the solution be very dilute, or the quantity of chlorine or of chloride very small, nitrate of silver will only produce a milkiness. This test is so delicate, that, according to Berzelius, 1 part of muriatic acid may thus be detected in above 113 million parts of water.—ED.

[2] If the substance under examination be in the state of solution, it should be tested with protosulphate of iron and sulphuric acid, or with quill-shavings, &c. (page 232). —ED.

CHAPTER VI.

COURSE OF QUALITATIVE ANALYSIS FOR COMPOUNDS WHICH ARE ABSOLUTELY INSOLUBLE, OR VERY SPARINGLY SOLUBLE IN WATER, BUT WHICH ARE SOLUBLE IN ACIDS, AND WHICH CONSIST ONLY OF A BASE COMBINED WITH AN ACID, OR OF A METAL COMBINED WITH A NON-METALLIC BODY, AND THE CONSTITUENT PRINCIPLES OF WHICH COMPOUND ARE AMONG THOSE OF THE LIST (Page 622).

* THE combinations belonging to this class are a great number of salts, especially almost all the neutral salts which *phosphoric, arsenic, carbonic,* and *boracic acids,* form with the *earths* and the *metallic oxydes,* properly so called, and consequently the bases from No. 4 to 25; for an excess of acid is necessary to dissolve these combinations combined with any of the four acids.

* When it has been ascertained that the compound under examination is completely insoluble, or at least very sparingly soluble in water, even though it be heated to ebullition, the water is to be decanted, and the operator must try to dissolve it by means of an acid. Muriatic acid is generally preferable to any other. The greatest number of the salts which are insoluble in water are soluble in this acid, especially with the help of heat.

The acid should be diluted with half its own bulk of water, and it is advisable not to employ a useless excess of it. *Nitric acid* should be substituted for *muriatic acid* for certain salts, especially those which have *oxyde of silver, suboxyde of mercury,* or *oxyde of lead* for a base.

* Among the compounds which are insoluble in water, are to be included the combinations of *sulphur* with the metals of the bases from No. 9 to 25, and also the metals of a few earths—although, as we have already mentioned it in page 454, several of these sulphurets are soluble in concentrated muriatic acid with disengagement of sulphuretted hydrogen, especially with the help of heat, yet nitric acid is generally resorted to in preference to muriatic acid for the purpose of dissolving them. It is evident that sulphurets, when thus treated, undergo decomposition, part of the sulphur being thereby converted into sulphuric acid, which may be discovered in the liquor, whilst another portion is separated with a colour which at first is not that of sulphur (page 453). The best manner of proceeding is to pulverise the sulphuret, digest it in nitric acid, and boil it until the operator is sure that the insoluble portion consists only of sulphur. It is true that sulphuret of lead forms, after treatment with nitric acid, a sulphate of lead which remains insoluble along with the sulphur, but in that case a sufficient quantity of lead is dissolved in the state of nitrate of lead to detect the metal in the solution by the appropriate re-agents. Sulphuret of mercury resists decomposition by nitric acid, wherefore in that case *aqua regia* is employed, which must also be resorted to for effecting the decomposition of sulphuret of tin or of antimony.

* Most of the combinations of sulphuric acid and of nitric acid with the above bases are soluble in water, except those mentioned in pages 624, 625. Several metallic oxydes, however, form with these acids neutral salts which are soluble, but their basic salts are insoluble in water and soluble in an acid.

1. METHOD OF PROCEEDING TO DETECT THE BASE OR THE METAL.

A. The acid solution of the salt which is insoluble in water is to be diluted with water, and then treated by *sulphuretted hydrogen water*. If a precipitate is produced, the base is one of those from No. 14 to 25, and is consequently the PEROXYDE OF

IRON, OXYDE OF CADMIUM, OXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, PROTOXYDE OF MERCURY, PEROXYDE OF MERCURY, OXYDE OF GOLD, PROTOXYDE OF TIN, PEROXYDE OF TIN, OF OXYDE OF ANTIMONY. To distinguish these oxydes from each other, the same method of proceeding is to be adopted as we have described from page 625 to page 628. We should remark here, that if the insoluble salt contains ARSENIC ACID, it is likewise precipitated from the solution by sulphuretted hydrogen in the state of sulphuret of arsenic. In most cases, however, it is easy to precipitate the metallic oxyde, which can be precipitated by sulphuretted hydrogen sooner than arsenic acid, because the latter requires some time to be precipitated by sulphuretted hydrogen, and it is only when heat is applied that it is precipitated quickly[1]. The oxybases, on the contrary, are precipitated sooner and with their characteristic colours, so that these precipitated metallic sulphurets can be collected rapidly upon a filter, after which the filtered liquor, which should smell strongly of sulphuretted hydrogen, must be boiled in order to see whether a precipitate of sulphuret of arsenic can be further produced. As a confirmation of the result obtained, the operator should never omit to examine the insoluble salt before the blow-pipe, in the manner described (page 337), in order to ascertain whether it contains arsenic acid or not.

B. If the solution of sulphuretted hydrogen produces no precipitate in the acid solution of the salt, the base of course is not one of those from No. 14 to 25, and in such case, the acid solution should accordingly be supersaturated with ammonia, and hydrosulphuret of ammonia added. If a black precipitate be then produced, or if a precipitate having already been produced whilst saturating the acid solution with ammonia, it is rendered black by addition of hydrosulphuret of ammonia, the base is one of those from No. 11 to 13, and is consequently PROTOXYDE OF IRON, OXYDE OF NICKEL, or OXYDE OF COBALT. To distinguish which of these three bases is contained in the salt, a small quantity of the solid salt must be tried before the blow-pipe, by which means OXYDE OF COBALT, if present, may be easily detected; but *protoxyde of iron* or *oxyde of nickel* is not so easily distinguished; and therefore, if the result be not quite satisfactory in reference to these two latter oxydes, a portion of the solution should be tested by *ferricyanide of potassium* (page 85).

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[1] With *arsenites*, however, this yellow precipitate is almost immediately produced by the addition of sulphuretted hydrogen, even in the cold solution, which precipitate may be recognised as being a sulphuret of arsenic, because it is soluble in hydrosulphuret of ammonia, and volatilisable at a high temperature. See the tests for arsenious acid, page 238. If PEROXYDE OF IRON be present, sulphuretted hydrogen will likewise cause a yellow or white precipitate of *sulphur*, which may be recognised as such by burning it, when the characteristic blue flame of burning sulphur and odour of sulphurous acid will at once identify it as such.—ED.

If the precipitate produced by hydrosulphuret of ammonia has the characteristic flesh-colour of the sulphuret of manganese, or if ammonia produces a precipitate which acquires this flesh-colour on the addition of hydrosulphuret of ammonia, then the base of the salt is PROTOXYDE OF MANGANESE.

* I have already remarked (page 64), that the flesh-colour of sulphuret of manganese may be concealed by very small quantities of other metallic sulphurets, especially those which are of a black colour.

If, on the contrary, the supersaturation of the acid solution of the salt by *ammonia* produces a white precipitate, the colour of which is not changed by addition of hydrosulphuret of ammonia, the base is either OXYDE OF ZINC or ALUMINA; yet *magnesia, lime, strontia,* and *baryta* may also be precipitated by ammonia when combined in the insoluble salt with *phosphoric acid,* or even with *boracic acid.* These substances may be distinguished from each other in the following manner:—

The presence of OXYDE OF ZINC may be recognised by mixing a small quantity of the insoluble salt with soda, and heating it on charcoal in the interior flame of the blow-pipe, or moistening it with solution of *nitrate of cobalt* (page 73), and then heating it in the flame of the blow-pipe. But if a considerable quantity of ammonia has been employed for the purpose of saturating the acid solution of the salt, the precipitate, if it be oxyde of zinc, is re-dissolved, and a clear liquid is thus re-produced, in which, however, *hydrosulphuret of ammonia* determines a white precipitate insoluble in potash and in ammonia.

The presence of ALUMINA is recognised by heating before the blow-pipe a small portion of the solid salt moistened with solution of *nitrate of cobalt,* and because the precipitate produced by saturating the acid liquid with ammonia is soluble in solution of excess of *potash* (page 44), and if hydrosulphuret of ammonia be added to this precipitate, it is nevertheless dissolved by an excess of *potash.*

The presence of STRONTIA and BARYTA is recognised, because dilute sulphuric acid produces a white precipitate in the acid solution of the salt diluted with a large quantity of water, or better still, because by adding to the liquor a solution of sulphate of lime, a precipitate of sulphate of baryta or of sulphate of strontia is produced, the first immediately, the second after some time[1]. In order to distinguish *baryta* from *strontia,* hydrofluosilicic acid is to be poured in the acid liquid diluted with water; and after some time, a precipitate will be produced if the salt contains BARYTA, but none will be produced by that re-agent if the base is STRONTIA.

The presence of LIME is ascertained by adding to the concentrated solution of the salt, first sulphuric acid and then alcohol. If a white precipitate be formed, the presence of LIME may be regarded as certain, provided the absence of *baryta* and of *strontia* has been previously ascertained.

The best method of detecting MAGNESIA in the solid salts which are insoluble in water, consists in treating them before the blow-pipe with solution of NITRATE OF COBALT (page 42) .

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[1] If oxalic acid be present, a white precipitate of oxalate of lime will be produced by solution of sulphate of lime ; if the muriatic acid solution contained *oxalate of lime,* a precipitate will have been produced when testing it with hydrosulphuret of ammonia.—ED.

[2] The pink colour produced by treatment of magnesia with nitrate of cobalt before the blow-pipe, takes place only if the magnesian salt is perfectly pure, for the smallest quantity of metallic oxydes prevents its production. Moreover, this fine pink colour is very feeble, and cannot be discriminated before the complete cooling of the

The absence of other earthy bases is already an indication that magnesia may be present.

C. If no precipitate has been produced in the acid solution of the salt by sulphuretted hydrogen, nor by hydrosulphuret of ammonia when added to the acid solution when first saturated with ammonia, the operator must add a solution of CARBONATE OF POTASH or OF SODA to the portion of the acid solution of the salt after first diluting it with water. If after saturation of the liquor with this alkali a precipitate is produced either immediately or after prolonged boiling, the base is one from No. 4 to 7, and is therefore either MAGNESIA, LIME, STRONTIA, or BARYTA.

To distinguish these substances from each other, a small quantity of dilute *sulphuric acid*, or better still, of *sulphate of lime*, must be added to the acid solution of the salt first diluted with water.

If a precipitate is produced, the base is either STRONTIA or BARYTA. The presence of the latter is recognised, because hydrofluosilicic acid, being poured in another portion of the acid and diluted solution of the salt, determines a white precipitate after some time.

LIME is recognised, if the above bases are not present, by adding a solution of muriate of ammonia[1], and saturating it with ammonia, and then testing with the solution of an oxalate, which will produce a white precipitate if LIME be the base of the compound (page 35)[2].

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substance, and a strong fire is required to develope it. The best way of insuring success consists in boiling the acid solution of the magnesian salt with potash, which base combining with the acid of the magnesian compound will determine a precipitate of magnesia, which may be collected upon a filter, washed with care to free it from the adhering potash, and then tested before the blow-pipe with nitrate of cobalt, as above said.—ED.

[1] We need hardly remark that this addition of muriate of ammonia is for the purpose of preventing the precipitation of magnesia in case it were present.—ED.

[2] The absence of baryta and of strontia must be previously ascertained before testing by solution of an oxalate, since oxalic acid and all the soluble oxalates produce in the neutral solutions of strontia and of baryta a white precipitate of oxalate of these bases, which is rendered more abundant still by the presence or further addition of ammonia.—ED.

If this reaction does not take place, *phosphate of soda* must be added to the same liquor in which the addition of the solution of an oxalate has proved the absence of lime. If a white precipitate is formed, although the liquor contains free ammonia, it is a conclusive proof of the presence of MAGNESIA (page 40).

D. It is useless to search for alkalies in the compound insoluble in water, since all these bases form with the acids in the list salts which are soluble in water.

2. COURSE OF THE ANALYSIS TO DETECT THE ACID OR THE NON-METALLIC BODY.

A portion of the dry salt is first to be moistened with water, and drenched with some dilute muriatic acid. The presence of CARBONIC ACID is recognised by an effervescence of an inodorous gas. If the carbonate insoluble in water is not in powder but in lumps, the application of heat is often required in order to determine that effervescence, and the acid employed should not be too concentrated. If dilute muriatic acid disengages with effervescence a gas having the odour of sulphuretted hydrogen, the compound under examination contains sulphur combined with a metal.

The insoluble compound is next thrown upon ignited charcoal in order to detect NITRIC ACID. This acid can be present only if the compound is a basic salt. The compound should likewise be tried before the blow-pipe upon charcoal in order to ascertain whether it contains ARSENIC ACID, which, however, if present, will have been detected in testing for the base of the salt.

The combination is next to be mixed in a platinum or porcelain crucible with *sulphuric acid* and *alcohol,* and if being set fire to it burns with a green flame, it indicates the presence of BORACIC ACID.

A portion of the combination is to be dissolved in *nitric acid,* if possible in the cold, and the acid solution diluted with water is tested with a little solution of *nitrate of silver*. If a white precipitate is formed, the substance under examination is a CHLORINE COMPOUND. But when the substance requires *aqua* *regia* for its solution, as is the case with subchloride of mercury, the presence of chlorine cannot be detected in this way. The substance, therefore, should be heated with a solution of ***potash*** which must be perfectly free from chloride of potassium, and the black precipitate of suboxyde of mercury produced may be collected upon a filter, after which the presence of chlorine in the liquor filtered therefrom may easily be detected by saturating it first with nitric acid, and testing it with nitrate of silver.

Nitric acid is poured upon a portion of the substance, and heat applied to the whole. If a reaction takes place accompanied with ruddy fumes of nitrous acid and separation of sulphur, which at first does not appear with its characteristic colour, but becomes visible by a prolonged digestion in nitric acid, and if the liquor being subsequently diluted with water yield a white precipitate[1] when tested by *nitrate of baryta*, the compound is a METALLIC SULPHURET. *Aqua regia* should be resorted to instead of nitric acid only if the combination is a SULPHURET OF MERCURY, because this substance is not acted upon by nitric acid. In this case the disengagement is not one of nitrous acid but of chlorine. If the combination is SULPHURET OF LEAD, of TIN, or of ANTIMONY, the reaction produced by digestion in nitric acid consists not only in sulphur, but in sulphate of lead, of tin, or of antimony. In these cases also *aqua regia* should be used instead of nitric acid.

* When sulphuret of lead is treated by nitric acid, the acid liquor contains scarcely any sulphuric acid, because this acid is precipitated in the state of sulphate of lead.

Lastly, to the *muriatic solution* of the salt diluted with water a solution of *chloride of barium* is added, or else a solution of

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[1] This white precipitate, it is almost superfluous to add, is sulphate of baryta; a portion of the sulphur of the sulphuret having been converted into sulphuric acid, the remainder of the sulphur forming, after a prolonged ebullition, hard yellow lumps, which however may be entirely converted into sulphuric acid by a very long digestion in nitric acid, which should be renewed several times; the entire conversion of the sulphur into sulphuric acid by this process is, however, a very tedious operation.—ED.

nitrate of baryta is poured in the *nitric acid* solution of the salt. If a white insoluble precipitate is produced, the acid of the compound is SULPHURIC ACID, which cannot exist in the compound except in the state of a basic salt. I have already said, that when the substance under examination is a combination of sulphur, and is treated by nitric acid or aqua regia, the acid solution contains sulphuric acid.

When the preceding experiments have failed in detecting the acid, then the compound must contain PHOSPHORIC ACID. Its presence especially in insoluble combinations is more difficult to find out than that of all other acids, in consequence of which a variety of experiments is always required to demonstrate it.

* If the compound contains a metallic oxyde, which can be precipitated either from its acid solution by *sulphuretted hydrogen*, or from its solution saturated or supersaturated with ammonia by *hydrosulphuret of ammonia*, and is consequently one of those from No. 15 to 25, or from No. 9 to 14; this oxyde is to be precipitated from its solution by sulphuretted hydrogen, or by hydrosulphuret of ammonia, and the presence of PHOSPHORIC ACID in the liquor filtered from the precipitates so obtained may be shown in the manner described (page 268). If PHOSPHORIC ACID be combined with an earth, its presence is still more difficult to detect. When this earth is *baryta*, *strontia*, *lime*, or *magnesia*, after having positively ascertained that this compound contains no arsenic or boracic acid, the operator is justified in concluding that PHOSPHORIC ACID is present if the muriatic acid solution yields a white precipitate with ammonia, provided it has been ascertained beforehand that it contains no metallic oxyde susceptible of being precipitated by sulphuretted hydrogen or by hydrosulphuret of ammonia (page 264).

* The most difficult case for the detection of phosphoric acid is when it is combined with alumina, because phosphate of alumina behaves with most re-agents like pure alumina (page 44). To

detect PHOSPHORIC ACID in *phosphate of alumina*, proceed as has been said (page 265)[1].

* The operator should never omit testing for phosphoric acid by the blow-pipe, according to the process set forth (page 270).

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[1] Dr. Fresenius directs phosphate of alumina to be dissolved in a small quantity of muriatic acid, and mixed with a rather large proportion of tartaric acid, and then to supersaturate the whole with ammonia. The presence of tartaric acid prevents phosphate of alumina from being precipitated by ammonia; and if a solution of sulphate of magnesia, or other soluble salt of magnesia, be added, a precipitate is produced, which is ammonio-phosphate of magnesia.—ED.

CHAPTER VII.

COURSE OF THE QUALITATIVE ANALYSIS OF COMBINATIONS WHICH ARE ALTOGETHER INSOLUBLE, OR VERY SPARINGLY SOLUBLE IN WATER AND IN ACIDS, AND WHICH CONSIST ONLY OF A BASE COMBINED WITH AN ACID, OR OF A METAL COMBINED WITH A NON-METALLIC BODY, THE CONSTITUENT PARTS BEING AMONG THE SUBSTANCES IN THE LIST, (page 622).

To the combinations which are insoluble, or very sparingly soluble in *muriatic acid, nitric acid,* and even *aqua regia,* the following substances only belong, namely:—SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, SULPHATE OF LEAD, CHLORIDE OF SILVER, and several ACID PHOSPHATES and ACID ARSENIATES, after having been strongly calcined.

With respect to the latter they can only be decomposed by boiling them with concentrated *sulphuric acid,* they then become soluble in water, provided their base is not *baryta, strontia, lime,* or *oxyde of lead.* They may be recognised by treatment before the blow-pipe, in order to ascertain whether they contain ARSENIC ACID or PHOSPHORIC ACID, the first of which is, however, more easily detected than the second.

With respect to the other combinations, they are all of a white colour except chloride of silver, which may often acquire a greyish-black, and after fusion, a yellowish colour. CHLORIDE OF SILVER and SULPHATE OF LEAD may be distinguished from SULPHATE OF LIME, of STRONTIA, and of BARYTA, because they (chloride of silver and sulphate of lead) turn black when *hydro-*

sulphuret of ammonia is poured upon them, especially if reduced into small lumps [or in powder], and all these substances may be distinguished from each other as follows:

A small portion of the combination under examination is to be gently heated in a small tube closed at one end over a small spirit-lamp. If it readily fuses, it is CHLORIDE OF SILVER. If it undergoes no change, it is SULPHATE OF LEAD. But in order to render this proof conclusive, the substance should be tried before the blow-pipe, by which means the presence of silver or of lead may be easily recognised (pages 100, 131).

If the substance when treated by *hydrosulphuret of ammonia* has undergone no change, then the base is either LIME, STRONTIA, or BARYTA combined with SULPHURIC ACID. These three bases are somewhat more difficult to distinguish from each other. The substance should be reduced to powder, and boiled with water, filtered, and the filtered liquid is divided into two portions. To one of these portions a solution of *chloride of barium* is added, and into the other portion a solution of an *oxalate*. If a white precipitate is formed in both portions, and that of the first portion is insoluble in acids, then the substance is SULPHATE OF LIME.

If nothing of the substance has dissolved by boiling with water, it is to be boiled (in the pulverised state) with a solution of *carbonate of potash* or *of soda*; the liquid portion is to be filtered and then supersaturated with muriatic acid, and, after dilution with water, *chloride of barium* is added. If an insoluble precipitate is then produced the combination is SULPHATE OF STRONTIA OR SULPHATE OF BARYTA. To distinguish these two salts from each other *muriatic acid* must be poured upon the insoluble part of the solution with *carbonate of potash* or of *soda*[1], in order to dissolve it; and after filtering, washing, and evaporating the filtered liquor to dryness, alcohol is to be poured upon the residuum and inflamed. If it burns with a carmine-red flame, the substance is SULPHATE OF STRONTIA. If not, it is SULPHATE OF BARYTA. The operator may also test the filtered liquid just spoken of by *hydrofluosilicic acid*. If a precipitate is formed after a time, it is owing to the presence of BARYTA. In the contrary case, the substance under examination is SULPHATE OF STRONTIA.

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[1] This insoluble portion is carbonate of baryta, or of strontia, produced by the exchange of base of the carbonate of soda, with which the sulphate of baryta, or of strontia, has been boiled as above.—ED.

CHAPTER VIII.

COURSE OF THE QUALITATIVE ANALYSIS OF MIXED COMPOUNDS WHICH ARE VERY SOLUBLE IN WATER, AND THE CONSTITUENTS OF WHICH BELONG TO THOSE IN THE LIST, (page 622).

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* The qualitative analysis of compounds, which contain several constituents, is much more difficult than that of simple compounds. It is absolutely necessary in such cases to adopt a systematic order in the different operations which such an analysis requires, because otherwise the operator would be exposed to overlook one or several of the constituents of the substances. It would be very difficult to indicate a method of proceeding for analysing qualitatively combinations supposed to contain all the substances which have hitherto been discovered. Such instructions, however, even if given, would prove of no practical value, because the description of the processes required would be too long and deficient in clearness, and thus confuse and dishearten the beginner. I have thought it best, therefore to take into consideration at first those constituents only which are of most frequent occurrence, after which I will show how by following an analogous course the rare substances may likewise be detected.

* For these reasons, I have in the three following chapters, supposed that the compound to be examined contains only the substances of the list (page 622).

* The analysis of mixed compounds is much less difficult when they are completely and easily soluble in water than when only partially soluble, or altogether insoluble in this menstruum.

* In these cases the use of the blow-pipe becomes very advantageous for the detection of such substances as produce reactions of a characteristic nature with this instrument.

* I have already said (page 624) that all the substances which I have enumerated, cannot exist at the same time in the combinations which are soluble in water. Thus, for example, in presence of the earths and of the METALLIC OXYDES, properly so called, that is to say, from No. 4 to 25, PHOSPHORIC, ARSENIC, BORACIC, and CARBONIC ACIDS, cannot exist; and *vice versâ,* these earths and metallic oxydes cannot exist in the presence of these four acids, since the salts which result from their mutual combinations are not soluble in water, and require the presence of a free acid for their solution. SULPHUR likewise forms with the metals of most of these bases compounds which are insoluble in water. I have said that SULPHURIC ACID produces insoluble compounds with some bases, and CHLORINE with the metals of certain bases.

* When the analyst has reason to think that the substance to be examined contains a great number of constituents, it is advisable, if possible, to operate upon larger quantities than in the case of mere simple compounds. By treating a portion of the solution, as will be shown hereafter, by solution of sulphuretted hydrogen, so much liquid is sometimes obtained that, test glasses being too small, ordinary glasses must be employed.

1. METHOD OF PROCEEDING TO DETECT THE BASE.

A. The concentrated aqueous solution of the salt is to be acidified a little, for which purpose *muriatic acid* is best. It is only when the compound contains *oxyde of silver, suboxyde of mercury,* or a great quantity of *oxyde of lead* (which may be perceived by the white precipitate which a few drops of muriatic acid will produce) that dilute *nitric acid* is substituted. Sulphuretted hydrogen is now added to the solution in sufficient quantity to make it smell strongly of the gas. If a precipitate is produced, especially by heating the whole, the bases are those from No. 15 to 25, that is to say, the compound may contain OXYDE OF CADMIUM, OXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, PROTOXYDE OF MERCURY, OXYDE OF GOLD, PROTOXYDE OF TIN, PEROXYDE OF TIN, and OXYDE OF ANTIMONY. The compound may also contain PEROXYDE OF IRON when that oxyde exists in the acid solution, in which case the addition of sulphuretted hydrogen gas precipitates sulphur. If a milky white precipitate of sulphur is formed in the acid solution, PEROXYDE OF IRON alone is present. If the compound contains ARSENIC ACID, the solution of sulphuretted hydrogen produces a yellow precipitate, if not immediately, at least after some time; but I have already said, that in presence of arsenic acid in a combination which is soluble in water, no metallic oxydes can exist, and therefore the base must be an alkali. If the acidified solution of the compound yields after some time, when heated with sulphuretted hydrogen water, a yellow precipitate soluble in hydrosulphuret of ammonia, the presence of arsenic acid, and consequently, if the combinations be neutral, the absence of metallic oxydes, properly so called, and of earths, may be regarded as certain.

The precipitate produced by sulphuretted hydrogen is allowed to settle, and the supernatant liquid is poured off as completely as possible, after which *ammonia* is poured on the precipitate, and then an excess of *hydrosulphuret of ammonia*, and a gentle heat is to be applied, but without boiling. If the precipitate redissolves completely in this re-agent, the combination may contain OXYDE OF GOLD, PROTOXYDE OF TIN, PEROXYDE OF TIN, and OXYDE OF ANTIMONY[1].

The solution in *hydrosulphuret of ammonia* is now to be diluted with water and decomposed by diluted *muriatic acid*[2]. The dissolved sulphurets are thereby precipitated with the characteristic colour, but mixed with sulphur in consequence of the decomposition of the hydrosulphuret of ammonia, a circumstance which gives a paler tinge to the precipitated sulphuret. If, however, the combination consists of several oxydes, the metallic sulphurets of which are soluble in hydrosulphuret of ammonia, they can be distinguished from each other in the following manner:

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[1] It is necessary to pour on the precipitate a great excess of hydrosulphuret of ammonia, and to leave the whole to digest for about fifteen or twenty minutes; for some of these bases (for example, protoxyde of tin) when thus converted into sulphurets require a very large excess of hydrosulphuret, and some time for their solution. It is also important not to forget to neutralise the precipitate with ammonia before adding the hydrosulphuret.—ED.

[2] No more muriatic acid need be added than will render the solution acid.—ED.

OXYDE OF GOLD is easily recognised by the production of a purple colour, when, after having diluted the original solution of the combination with a large quantity of water, it is mixed with a few drops of *protochloride of tin* previously rendered clear by the addition of free muriatic acid (page 170). The presence of gold may also be recognised by testing the original solution with *protosulphate of iron*, by which metallic gold is thrown down in the state of a brown precipitate.

PROTOXYDE OF TIN is recognised, because in many cases the combination, upon being diluted with a large quantity of water, yields a milky solution; but principally because, after diluting the original solution with a very large quantity of water, the addition of a dilute solution of chloride of gold produces a purple colour[1].

PEROXYDE OF TIN and OXYDE OF ANTIMONY are more difficult to detect when accompanied by other metallic oxydes, the metallic sulphurets of which are soluble in hydrosulphuret of ammonia. Their presence can be best demonstrated by the behaviour of the sulphurets formed before the blow-pipe. The presence of OXYDE OF ANTIMONY may also be detected, because the muriatic solution of the combination becomes milky by addition of a large quantity of water[1], when the solution does not contain too much free acid. If, on the contrary, only one of these oxydes is present, unaccompanied by any oxyde of other metals, the sulphuret of which is soluble in hydrosulphuret of ammonia, it is recognised principally by the characteristic colour of the sulphurets.

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[1] Protosalts of tin cannot always be detected in mixed compounds by perchloride of gold, and vice versâ. If, for example, the original solution of the compound contains at the same time a *protosalt of iron*, and a *protosalt of tin*, testing it with perchloride of gold will be of no avail, since protoxyde of iron gives a blue or a brown precipitate, or a purple one, according to the state of dilution, with perchloride of gold, and the like reaction is also produced with protoxyde of tin; it is therefore impossible to detect the presence of protoxyde of tin by testing with perchloride of gold, if a protosalt of iron exists at the same time in the solution. The same inadvertence has happened to Dr. Fresenius and to M. Parnel in their excellent works on chemical analysis, both recommending, like H. Rose, to test the original solution with *perchloride of gold*. But since the precipitate formed by that re-agent in solutions of protosalts of iron and of tin, when existing simultaneously in the dissolved state, is not characteristic of either metal; perchloride of gold cannot be said to be the appropriate test. If these two compounds *only* exist in the solution, sulphuretted hydrogen will at once precipitate the tin in the state of a dark brown sulphuret, and will leave the protosalt of iron untouched; but we are speaking here of mixed compounds, containing, for example, *protoxyde of tin*, *protoxyde of iron*, and *protoxyde of antimony*. We have given further on, the means of qualitatively determining such compounds.—ED.

When the precipitate produced in the acid liquor by solution of *sulphuretted hydrogen* is not completely dissolved by *hydrosulphuret of ammonia,* or is altogether insoluble in it, the combination may contain OXYDE OF CADMIUM, PROTOXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, and PROTOXYDE OF MERCURY. That the precipitate produced by sulphuretted hydrogen is insoluble in hydrosulphuret of ammonia, is ascertained, because after digestion of the precipitate in the re-agent, and dilution with water, an excess of muriatic acid poured in the liquor filtered from the insoluble residuum produces no milkiness or turbidness of liberated sulphur, and does not precipitate a metallic sulphuret. Or the following method is still more easy: after digestion in hydrosulphuret of ammonia, put a few drops of the filtered liquid upon a strip of platinum foil, and evaporate to dryness by means of the spirit-lamp, and if after heating the foil to redness no residuum is left, then the re-agent has not dissolved anything.

The precipitated metallic sulphuret is gathered upon the smallest possible filter, and well washed, after which it is treated with pure *nitric acid.* Generally it is not necessary in qualitative analysis to separate the precipitate from the filter, and it may be digested along with the filter and the nitric acid in a test glass; * but when the quantity of the precipitate is considerable, it is better to remove it from the filter with a blade of platinum, and digest it in nitric acid without the paper. Metallic sulphurets are decomposed by nitric acid with the help of heat; the metal becoming oxydised dissolves, and sulphur is separated, and after a prolonged digestion it appears with its characteristic yellow colour. When this has taken place, the liquor is filtered to separate it from the undissolved sulphur[1].

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[1] So does solution of protoxyde of tin.—ED.

Sulphuret of mercury, however, is an exception. It is almost insoluble in nitric acid, except it be very strong. This sulphuret remains undissolved, with its peculiar colour, which in this case is black. It should then be tested before the blow-pipe, by which means the presence of mercury may be very easily recognised, and which may exist in the solution of the compound in the state of suboxyde, or of protoxyde of mercury. If it exists in the compound in the state of protoxyde, the sulphuret obtained by treatment with sulphuretted hydrogen sublimes without decomposition or change, when heated in a small tube closed at one end. If it be in the state of suboxyde, the sublimed sulphuret is mingled with globules of metallic mercury.

Besides *sulphur* and sulphuret of mercury, a small quantity of *sulphate of lead* may also remain undissolved if the compound contained protoxyde of lead, which will have precipitated with the other sulphurets in the state of sulphuret of lead. But the greatest part of the protoxyde of lead is always dissolved by the nitric acid.

When an excess of *ammonia* being poured in the liquid filtered from the sulphur communicates a blue colour to the solution, it indicates the presence of PROTOXYDE OF COPPER.

If a little *muriatic acid* being added to another portion of the liquor produces a white precipitate which does not disappear by dilution with a large quantity of water, but which is soluble in ammonia, the combination contains OXYDE OF SILVER, which, however, may be ascertained at the beginning of the analysis by testing the original solution with muriatic acid, which will have produced a white precipitate.

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[1] Stirring the mass whilst boiling promotes the solution, and prevents spirting.—ED.

Dilute *sulphuric acid* is added to another portion of the liquor diluted with water; if a white precipitate is thereby determined, the combination contained PROTOXYDE OF LEAD, the presence of which in concentrated solutions will likewise have been recognised from the beginning by the formation of a white precipitate upon adding muriatic acid.

Another portion of the liquid is evaporated in a very small porcelain dish, so as to dissipate the greatest part of the nitric acid[1], a few drops of muriatic acid are now added, and then a large quantity of water. If a white precipitate is produced, the combination contained OXYDE OF BISMUTH.

The presence of OXYDE OF CADMIUM in the combination is recognised by mixing the precipitated metallic sulphurets with soda, and heating upon charcoal in the interior flame of the blow-pipe. A brown coating is then observed, which must not be confounded with that produced by the combinations of lead, and of bismuth, when treated in the same manner (page 95)[2].

B. The liquid separated from the metallic sulphurets which were precipitated from the acidified solution of the compound by sulphuretted hydrogen, is treated as if sulphuretted hydrogen had produced no precipitate in this acid liquor. The first step to be taken, however, consists in examining whether it still contains any fixed bases. For this purpose a few drops of it are evaporated upon a strip of platinum foil heated to redness. If nothing remains, the liquor contains no fixed bases; if, on the contrary, a residuum is left, the examination of the liquid must be continued. With this view the acidified solution is supersaturated with ammonia, and hydrosulphuret of ammonia is added to the ammoniacal liquor. If a precipitate is formed, it is owing to the presence of PEROXYDE OF IRON, PROTOXYDE OF IRON, OXYDE OF NICKEL, OXYDE OF COBALT, OXYDE OF ZINC, PROTOXYDE OF MANGANESE, and ALUMINA.

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[1] The nitric acid must be evaporated as much as possible, because the neutral or basic salts of bismuth only are insoluble, but they dissolve readily in an excess of acid. In a solution too acid or not sufficiently evaporated, no milkiness is produced by addition of water.—ED.

[2] The difference of behaviour of the combinations of lead, bismuth, and cadmium, mixed with soda upon charcoal before the blow-pipe, may be seen at one glance, thus:—

Lead.—Charcoal is covered with *yellow coating* easily reduced into *metallic lead* which may be *flattened* under the hammer.

Bismuth.—Charcoal covered with *yellow coating* reducible into *metallic bismuth, brittle* under the hammer.

Cadmium.—Charcoal covered with *reddish-brown* coating *cannot be reduced into the metallic state.*

The precipitate obtained is filtered and washed with water, to which a few drops of hydrosulphuret of ammonia have been added, and digested together with the filter with a little dilute *muriatic acid* in a test glass, until all odour of sulphuretted hydrogen has disappeared. The liquor is then filtered and heated with a little nitric acid. [* It is not advisable to treat the precipitate on the filter with nitric acid, or aqua regia, instead of muriatic acid, because the action of these acids upon the paper would introduce an organic matter, the presence of which might modify the behaviour of the re-agents towards the dissolved oxydes]. If the precipitate is not completely decomposed and dissolved by muriatic acid, which is the case when SULPHURET OF NICKEL, or SULPHURET OF COBALT, is present amongst the metallic sulphurets precipitated by hydrosulphuret of ammonia; it is to be removed from the filter, and digested with nitric acid, or else after having used muriatic acid, some nitric acid is further added.

* In reference to the precipitation of OXYDE OF NICKEL by means of *hydrosulphuret of ammonia* in qualitative analysis, I must remark that sulphuret of nickel is not completely insoluble in an excess of the re-agent, and the supernatant liquid retains a slight black tinge (page 81). Yet this effect takes place only when sulphuret of nickel is precipitated alone, and not conjointly with other metallic sulphurets, for in that case it is completely separated by this re-agent.

An excess of *ammonia* is poured in the acid liquor, the precipitate produced is collected on a filter, and washed. It may consist of PEROXYDE OF IRON and ALUMINA[1]. If the precipitate be white, it is ALUMINA alone; if *brown*, the two bases may exist simultaneously. But to remove all doubt in this respect, it is to be dissolved, without removing it from the filter, by a little *muriatic acid,* filtered, and an excess of pure *potash* added. Peroxyde of iron is thereby precipitated, if present, whilst the alumina is dissolved. *Muriate of ammonia* may now be added to the filtered liquor, which produces a white precipitate, if the solution contains ALUMINA. The PEROXYDE OF IRON which has been detected may have existed in the compound in the state of PROTOXYDE OF IRON. To ascertain this, solution of *perchloride of gold* is added to the original solution. If a brown powder of metallic gold is thus produced, it is a proof that the compound contained PROTOXYDE OF IRON[1].

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[1] The acid liquor should contain enough acid to produce with the ammonia a

If the liquor filtered from the precipitate produced by ammonia is of a blue colour, the operator may conclude that it contains OXYDE OF NICKEL. If it is of a slight pink colour, OXYDE OF COBALT existed in the compound. Besides, OXYDE OF COBALT, even in the smallest possible quantity, and though mixed with several other metallic oxydes, is easily recognised before the blow-pipe by its property of imparting an intense blue colour to glass of borax or of microcosmic salt, both in the exterior and in the interior flame (page 78).

The ammoniacal liquor is mixed with a solution of pure *potash.* If a light apple-green precipitate is formed, the combination contains OXYDE OF NICKEL. If the precipitate has another colour, and turns brown by exposure to the air, the combination contains PROTOXYDE OF MANGANESE, the presence of which may be conclusively proved before the blow-pipe (page 65).

The liquid filtered from the precipitate produced by potash is precipitated by hydrosulphuret of ammonia. The precipitate is roasted a little upon charcoal before the blow-pipe, after which the presence of OXYDE OF COBALT, OXYDE OF ZINC, and PROT-

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sufficient quantity of ammoniacal salt, otherwise *magnesia,* if present, would be precipitated. If the solution does not contain much acid, muriate of ammonia should be added before the ammonia.—ED.

[1] Same remark as before if protoxyde of tin is present.—ED

OXYDE OF MANGANESE may be easily detected by means of the blow-pipe.

C. The liquor which was filtered from the precipitate produced by hydrosulphuret of ammonia, after supersaturating the acid solution of the compound with ammonia, still remains to be examined. For this purpose, the first step consists in ascertaining whether it contains any fixed bases. This is done by evaporating a few drops of it upon platinum foil heated to redness. If nothing remains, no further test needs be resorted to for demonstrating the absence of fixed bases, since this is sufficient proof that the liquor contains none; but if a residuum be left on the platinum foil, the liquor may still contain MAGNESIA, LIME, STRONTIA, BARYTA, SODA, and POTASH.

The liquor is then supersaturated with muriatic acid, in order to decompose the excess of hydrosulphuret of ammonia which was previously added to it, and heat is applied until all odour of sulphuretted hydrogen has vanished, and it is filtered from the sulphur which this treatment will have precipitated. An excess of solution of carbonate of ammonia is now added, and heat applied to the whole, in order to expel the free carbonic acid. The precipitate produced thereby may consist of LIME, STRONTIA, and BARYTA.

The precipitate is dissolved in muriatic acid, and a few drops of very dilute sulphuric acid are added to the solution, or better still, a somewhat dilute solution of sulphate of potash. If a precipitate is immediately produced, the three earths may exist in the liquor; but if the liquor becomes turbid only after a time, it contains LIME only. In the first case a very slight excess of dilute sulphuric acid is added to a portion of the liquor, the whole is heated, and the precipitate is separated by filtering. The filtered liquid is now to be slightly supersaturated with *ammonia*, and then a solution of *oxalic acid* or of an *oxalate* is added. If a white precipitate is obtained after a little time, it is a sign of the presence of LIME; but if no precipitate is formed, the absence of this earth may be looked upon as certain.

The precipitate produced by sulphuric acid may contain

BARYTA and STRONTIA, either separately, jointly, or even mixed with LIME, if the presence of the latter earth has been detected in the filtered liquor.

* In order to ascertain this, *hydrofluosilicic acid* must be poured in another portion of the muriatic acid solution of the earths. If after some time a precipitate is produced, it is a sign of the presence of baryta. This precipitate must be separated by filtering, and *sulphate of potash* is added to the liquor filtered therefrom. If a precipitate is produced, it is a proof that, besides baryta, it contained likewise *strontia* either alone or mixed with LIME.

* Another trustworthy method for the determination of the precipitate of the alkaline earths produced by carbonate of ammonia is the following:—The precipitate is dissolved in muriatic acid and solution of SULPHATE OF LIME is added to the liquor. If no turbidness appears, even after a long time, the precipitate contained *lime* only, the presence of which may be immediately recognised by means of other re-agents poured in fresh portions of the liquid. If the solution of *sulphate of lime* produces a precipitate, the three earths may exist in the muriatic acid solution; if a precipitate appears immediately, the presence of BARYTA is probable; and if it appear only after a time, the presence of STRONTIA may be suspected. Hydrofluosilicic acid being added to a portion of the muriatic acid solution demonstrates conclusively the presence or absence of BARYTA; should, however, this earth be present, the liquid is to be filtered from the silicifluoride of barium (after having given the precipitate the time necessary for its complete deposition), or if absent, the liquor itself must be evaporated to dryness after addition of sulphuric acid; the evaporation must be carried on towards the end in a platinum crucible. The dry mass is then treated by water and left for a long time in contact with it and then filtered. If the addition of the solution of an *alkaline oxalate* produces a precipitate in the filtered liquor, and if *chloride of barium* (supposing that the excess of sulphuric acid has been entirely expelled from the dry mass) being added to

another portion of the same liquor, produces likewise a precipitate, the combination contained STRONTIA and LIME; the absence of which is demonstrated when both the oxalates of alkalies and chloride of barium fail in producing a precipitate in the filtered liquor.

After the precipitation of the LIME, or STRONTIA, or BARYTA, by carbonate of ammonia, the liquor filtered from the precipitate may still contain MAGNESIA, SODA, or POTASH.

* This may also be the case even though the solution of carbonate of ammonia may have produced, no precipitate in the muriatic acid solution.

In the first case the operator must not omit to evaporate to dryness upon a platinum foil a few drops of the liquor which has been filtered from the earthy carbonates, and to heat the platinum foil to redness in order to ascertain whether a fixed residuum is left; for if nothing remains, it is useless to look for more fixed bases.

* On this occasion it is well to remark, that when the filtered liquor contains only alkalies in the state of metallic chlorides, if the operator does not proceed with due care in evaporating the few drops of the liquor, as just said, the minute quantity of chlorides of alkalies in these drops may be easily volatilised; which is less liable to take place when a certain quantity of the liquor is evaporated in a platinum crucible, and heating it to redness towards the end, the crucible being half covered over[1].

The presence of the two FIXED ALKALIES and of MAGNESIA may be ascertained by pouring solution of *phosphate of soda* in a portion of the liquor. If this re-agent produces, after some time, a white precipitate, it is a proof of the presence of MAGNESIA, but POTASH and SODA may also exist simultaneously with this alkaline earth in the liquor.

* If there be no MAGNESIA, and consequently if no precipitate is produced, another portion of the liquor, in which no phosphate

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[1] It is therefore advisable, first to concentrate a portion of the liquid, and then to take from that concentrated portion a few drops which are afterwards evaporated on platinum foil or in a crucible, as directed.—ED.

of soda has been added, must be evaporated to dryness, and the residuum heated to redness in a platinum crucible until all ammoniacal salts are volatilised; then the greatest portion, but not all, of the calcined residuum is dissolved in a very small quantity of water, a little alcohol is added to the liquor, and then a little alcoholic solution of chloride of platinum. If a yellow precipitate is produced, it is a proof that the combination contained POTASH; but if no precipitate is formed, then SODA must be present, provided the absence of MAGNESIA has been ascertained, and provided, of course, that it has been proved that the liquor filtered from the earthy carbonates contains still a fixed constituent. The presence of *soda* is, however, very easily detected, even when the quantity of potash is much more considerable than that of the soda, by examining a portion of the calcined residuum before the *blow-pipe* upon a platinum wire. If the exterior flame has a violet colour, POTASH only is present, but if it becomes intensely yellow, SODA is present either alone or conjointly with POTASH; the existence of the latter, however, has already been demonstrated by treatment with *chloride of platinum*. We have said on a former occasion (page 13), that in certain cases the platinum wire alone may communicate a feeble yellow tinge to the flame.

If, however, the liquor filtered from the earthy carbonates really contains MAGNESIA, which may be easily ascertained by means of a solution of phosphate of soda, the ulterior operations of the analysis are rendered more difficult. For this purpose another portion of the muriatic acid solution, to which no phosphate of soda has been added, is taken for examination.

* When the operator positively knows that the bases contained in the substance in process of analysis are in the state of metallic CHLORIDES or of NITRATES (which is detected by the other part of the analytical course for the detection of acids), and when during the various operations performed no other acid but muriatic or nitric acid has been used (but no sulphuric acid), it is only necessary to evaporate the liquor to dryness in a porcelain dish, after which the residuum must

be strongly ignited and for a long time in contact with the air, either in a small platinum crucible, or, if nitrates be present, in a small porcelain crucible. In the latter case the decomposition of the nitric acid can be promoted by adding gradually and cautiously to the fused mass a small quantity of some kind of organic matter free from fixed principles, by which means deflagration is produced. After calcining, the residuary mass is treated by water. If before ignition it contained only metallic chlorides, the calcining it in contact with the air has partly decomposed the chloride of magnesium and liberated the magnesia which is combined with some as yet undecomposed chloride of magnesium; the quantity of the latter is very inconsiderable when the dried mass has been heated several times in the platinum crucible, taking care at each time to moisten it with a little water, and to place upon it a small piece of carbonate of ammonia. Treating the mass with water leaves the magnesia undissolved, whilst the alkalies are dissolved thereby in the state of metallic chlorides, and remain in the filtered liquor which may now contain either chloride of potassium, or of sodium, or both simultaneously. This may be detected in the manner described just above.

Yet if before calcining, the mass was composed of NITRATES, the action of the fire will have converted the nitrate of magnesia into pure magnesia, which is insoluble in water, whilst the alkalies in the state of nitrites or of carbonates dissolve in the liquid, and may be recognised in the liquor filtered from the magnesia.

* But when the bases are combined with sulphuric acid in the substance under examination, the process must be altogether modified; for sulphate of magnesia, like the sulphates of alkalies, cannot be decomposed by calcining. It is hardly possible, however, if magnesia is present, that very soluble substances can contain other combinations than sulphates, nitrates, or metallic chlorides. If it contains sulphuric acid, the liquor should be evaporated to dryness and the residuum ignited, in order to volatilise the ammoniacal salts which have been formed during

the operation. If the compound under examination contains not only *sulphates*, but *nitrates* and metallic *chlorides* also, a little sulphuric acid is added to the ignited mass, and the excess of this acid must be volatilised by a moderate ignition. The residuum is then dissolved in water, and an excess of *acetate of baryta* is added to this solution, by which means the sulphuric acid is precipitated in the state of sulphate of baryta. The liquor filtered from this precipitate contains the excess of *acetate of baryta*, ACETATE OF MAGNESIA, and the *alkalies*, if any, combined with acetic acid. The solution is evaporated to dryness, and the dry residuum ignited in a small porcelain capsula, or better still, in a platinum crucible. After ignition, water is poured upon the residuum, *carbonate of baryta* and CARBONATE OF MAGNESIA, or, if the mass has been strongly ignited, pure MAGNESIA remains insoluble, whilst the *alkalies*, if any are present, are dissolved in the state of carbonates. The presence and nature of the alkalies may then be easily detected in the solution, especially after converting them into the state of chlorides by addition of muriatic acid.

D. It is impossible by following these methods to detect the presence of AMMONIA. This substance is detected by pouring solution of pure potash upon a portion of the compound under examination, and slightly heating the whole; an odour of ammonia is then disengaged, and a glass rod moistened with muriatic acid held at the surface of the liquid produces white fumes if AMMONIA is present[1].

2. METHOD OF PROCEEDING TO DETECT THE ACIDS.

A portion of the concentrated solution of the compound is first treated with dilute muriatic acid in order to ascertain by the effervescence produced whether CARBONIC ACID or SULPHUR are present. If the gas disengaged with effervescence is inodorous, it is CARBONIC ACID; if, on the contrary, it exhales the well-known odour of sulphuretted hydrogen, the combination contains SULPHUR in the state of *metallic sulphuret*. In the latter case, however, it may also contain carbonic acid, the presence of which will be subsequently detected.

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[1] It has been remarked by Dr. Fresenius, that solution of potash emits, whilst boiling, ammoniacal vapours, which may lead to error; and therefore it is sometimes better to triturate the substance with hydrate of lime and water instead of boiling it with solution of potash.—ED.

Into another portion of the solution of the combination which must be neutral, or, at least, not acid, a solution of *chloride of barium* is poured. (Instead of a solution of *chloride of barium* one of nitrate of baryta is used, if the solution contains PROTOXYDE OF LEAD, OXYDE OF SILVER, or SUBOXYDE OF MERCURY). If a precipitate is produced, the combination may contain SULPHURIC, PHOSPHORIC, ARSENIC, and BORACIC ACIDS; and when CARBONIC ACID is present, it also yields a precipitate with a solution of *chloride of barium*.

Dilute *muriatic acid* is next added to the precipitate produced, or else dilute *nitric acid*, if *nitrate of baryta* has been employed. If, after the addition of a certain quantity of water, this acid dissolves the precipitate produced by the barytic salt, it is a proof that the combination contains no SULPHURIC ACID. If the precipitate dissolves with effervescence, and does not reappear when the acid solution,—which, however, must contain the least possible quantity of free acid,—is boiled and saturated with *ammonia*, the precipitate produced by the barytic salt is due to the presence of CARBONIC ACID, which, however, may have been detected before.

* If, however, the solution of the barytic salt has precipitated BORACIC ACID, borate of baryta cannot, in most cases, be precipitated from an acid solution by ammonia; because it is soluble in solutions of ammoniacal salts, of chloride of barium, and other salts[1].

If the precipitate dissolves with effervescence in the acid and reappears by saturating the liquor with ammonia, the combination contained carbonic acid in conjunction with one or more of the acids which have been mentioned. If this, however, does not take place, the combination may still contain PHOSPHORIC and ARSENIC ACIDS, or even, though this is not likely, BORACIC ACID.

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[1] Carbonic acid, however, forms a precipitate of carbonate of baryta in the solution of borate of baryta.—ED.

The presence of ARSENIC ACID is detected by means of a solution of *sulphuretted hydrogen.* No metallic oxyde can disguise the colour of the precipitate produced by this re-agent; for when arsenic acid is present, alkalies only can accompany it, because the earths and the metallic oxydes form with *arsenic acid* compounds which are insoluble in water, except they contain an excess of acid. It is easier still to detect the presence of *arsenic acid* by means of the blow-pipe.

The presence of BORACIC ACID is recognised by adding sulphuric acid and alcohol to the compound.

PHOSPHORIC ACID is much more difficult to detect. After having ascertained the absence of *arsenic* and *boracic acids*, the presence of phosphoric acid is shown by the precipitate which a solution of chloride of barium or of chloride of calcium produces in the concentrated solution of the compound, which precipitate disappears by the addition of muriatic or of nitric acids, and which re-appears by saturating the liquor with ammonia. But if all or some of the above acids, or only one of them be present, it is necessary to resort to another method, in order to detect phosphoric acid.

If, of all the above acids, ARSENIC ACID alone is present, it may be separated by means of a solution of *sulphuretted hydrogen.* The liquor should be previously rendered acid, and sulphuretted hydrogen added in sufficient quantity to exhale a strong odour of that gas. The whole is then to be boiled, and the sulphuret of arsenic produced is separated by filtering. The presence or absence of PHOSPHORIC ACID may now be easily ascertained in the filtered liquid totally free from sulphuretted hydrogen, by saturating it and then pouring into it a solution of *chloride of barium* or of *calcium.* If, however, BORACIC ACID is present at the same time, PHOSPHORIC ACID may already be distinguished, because the precipitate produced by the solution of chloride of barium or of chloride of calcium does not disappear by the addition of a very large quantity of water, neither does it dissolve in very small quantities of solutions of ammoniacal salts, of chloride of barium, of chloride of calcium, and other salts, which would take place if boracic acid alone was present.

* In many cases, the best way of detecting PHOSPHORIC ACID, after having separated the arsenic acid which may exist in the compound, consists in the use of *nitrate of silver*, with the precautions indicated (page 262). It is especially important after the elimination of the arsenic acid to free the liquor completely from sulphuretted hydrogen, for without this precaution the addition of solution of nitrate of silver might produce a black precipitate of sulphuret of silver.

If a solution of *chloride of barium* has produced in the concentrated solution of the combination a precipitate which the addition of muriatic acid or of nitric acid does not cause to disappear, or dissolves only partially, the combination contains SULPHURIC ACID. If the liquor filtered from this precipitate of sulphate of baryta be treated as has just been said, the operator may ascertain whether the combination further contains any ARSENIC, PHOSPHORIC, or BORACIC ACIDS.

The presence of a COMBINATION OF CHLORINE is detected, when a solution of *nitrate of silver*, poured in the solution of the substance under examination, produces a white precipitate insoluble in dilute nitric acid.

Lastly, the presence of NITRIC ACID is recognised by throwing a little of the combination upon ignited charcoal, which will produce a deflagration, if nitric acid be present. The other methods, already mentioned (page 235), for the detection of that acid, should be likewise resorted to.

CHAPTER IX.

COURSE OF THE QUALITATIVE ANALYSIS OF MIXED COMPOUNDS WHICH ARE ONLY PARTIALLY SOLUBLE, OR ALTOGETHER INSOLUBLE IN WATER, BUT SOLUBLE IN ACIDS, AND THE CONSTITUENTS OF WHICH ARE AMONG THE SUBSTANCES IN THE LIST, (Page 622).

* Among the combinations belonging to this chapter are those mentioned (page 635). All the alloys formed of the metals of the bases (page 622) may be examined in the same manner.

The combination to be examined is first treated by water. If it dissolves partially, the solutions thus obtained must be subjected to the treatment described in the preceding chapter. If it is insoluble in water, it is to be dissolved in muriatic acid, or, if it contains *protoxyde of lead, oxyde of silver*, or *suboxyde of mercury*, in nitric acid. The solution is promoted by the application of heat, especially if METALLIC SULPHURETS are present. In this case, it is often advantageous to employ *aqua regia*, which, as we have already said (page 542), attacks compounds on which muriatic and nitric acids alone have no action.

The portion of the compound which remains undissolved after treatment with water is to be treated in the same manner as the substances which are altogether insoluble in water.

* Alloys are generally soluble in nitric acid. A few dissolve likewise in muriatic acid; others, again, are soluble only in *aqua regia*. This is known from the solubility of the isolated

metals in the various acids, which subject has been treated of in the Third Chapter of the First Part of this volume.

1. METHOD OF PROCEEDING TO DETECT THE BASES.

The method of proceeding to detect the bases in the acid solutions is very similar to that which I have indicated in Chapter VIII., for the analysis of the combinations which are soluble in water. It is necessary, however, to modify it a little, because in the preceding case, it was unnecessary to pay any attention to the earths or to the metallic oxydes, properly so called, when PHOSPHORIC, ARSENIC, CARBONIC, and even, in certain cases, BORACIC ACIDS were present; since the very presence of these acids was in itself a sufficient indication of the absence of earths and metallic oxydes by the insolubility in water of the compounds resulting from the union of these substances. For the same reason, it was unnecessary to look for SULPHUR, when metallic oxydes, properly so called, existed in the combination.

A. To the acid solution of the compound, one of sulphuretted hydrogen is added, and the precipitate resulting therefrom is subsequently to be treated by hydrosulphuret of ammonia in the manner mentioned (page 652). If the combinations contain any ARSENIC ACID, this acid is likewise precipitated by the solution of sulphuretted hydrogen, and the sulphuret of arsenic produced dissolves in hydrosulphuret of ammonia. If PEROXYDE OF TIN and OXYDE OF ANTIMONY exist also in the liquor at the same time, it is often difficult to detect with certainty the presence of these three substances. In this case that of ARSENIC ACID is easily recognised by treating the substance with soda upon charcoal before the blow-pipe. That of OXYDE OF ANTIMONY is exhibited by the orange-yellow colour of the precipitate which is produced when the dilute solution of the metallic sulphurets in hydrosulphuret of ammonia is decomposed by dilute *muriatic acid.* But in presence of these two substances it is more difficult to determine whether PEROXYDE OF TIN exists or not in the compound. In such a case the best way is to dry the metallic sulphurets which dilute muriatic acid has precipitated from the dilute solution in hydrosulphuret of ammonia, and then to heat them strongly and as much as possible out of the contact of the air in a glass tube closed at one end, during which operation sulphur and sulphuret of arsenic are sublimed, and sulphuret of tin and sulphuret of antimony remain behind in the lower degree of sulphuration. This residuum is dissolved in concentrated muriatic acid with the help of heat. The solution is diluted with water, and it contains then oxyde of antimony, and if peroxyde of tin existed in the solution, it now exists in the solution in the state of protoxyde of tin, which may then be easily detected by solution of perchloride of gold.

If the metallic sulphurets precipitated from the acid solution of the combination by that of sulphuretted hydrogen are not entirely dissolved, or even remain insoluble in hydrosulphuret of ammonia, the combination may further contain OXYDE OF CADMIUM, PROTOXYDE OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, and PROTOXYDE OF MERCURY. These metals may be recognised precisely in the manner which has been indicated in the preceding chapter, (page 652).

B. The liquor separated from the precipitate which the solution of sulphuretted hydrogen has produced, is next treated as has been said in the preceding chapter, in order to ascertain whether it still contains any fixed bases. If so, the solution is to be saturated with ammonia, and hydrosulphuret of ammonia is next added. The precipitate which is produced may be owing to the presence of PEROXYDE OF IRON, PROTOXYDE OF IRON, OXYDE OF NICKEL, OXYDE OF COBALT, OXYDE OF ZINC, PROTOXYDE OF MANGANESE and ALUMINA; but this precipitate may also contain MAGNESIA, LIME, STRONTIA, and BARYTA, when these bases are combined with *phosphoric*, or with *boracic* acids. This precipitate must first be treated almost in the same manner as has been indicated in the preceding chapter for the examination of the bases precipitated under similar circumstances. It is digested in *muriatic acid* or in *aqua regia*, and in the first case the filtered solution is treated with nitric acid.

Dilute *sulphuric acid* is added to the liquor. If it contains

STRONTIA and BARYTA, these bases are completely precipitated, if not immediately, at least after a short time, in the state of sulphate of baryta, or of strontia. LIME is also partly precipitated when it is abundant, and provided the solution be not too dilute. The precipitate is collected on a filter without washing, and then treated by a large quantity of water. If nothing is dissolved, it consists only of *sulphate of baryta* or of *strontia*, but if it is partially dissolved, the baryta and strontia may be accompanied by LIME. The presence of LIME is very easily detected in the filtered liquor by pouring a solution of an oxalate. The undissolved residuum, which may consist of *sulphate of baryta* and of *strontia*, is then treated by a solution of *carbonate of potash* or of *soda*, as has been said in the preceding chapter (page 640).

The acid liquor filtered from the earthy sulphates is supersaturated with ammonia. This re-agent precipitates more especially PEROXYDE OF IRON and ALUMINA, but it can likewise produce a precipitate of MAGNESIA, if the liquor contains phosphoric acid. The precipitate is boiled with a solution of *potash*, which leaves the PEROXYDE OF IRON and MAGNESIA untouched, and they lose the greater part of their phosphoric acid, whilst the ALUMINA is dissolved and may be re-precipitated from the solution by muriate of ammonia. Before the *blow-pipe*, the presence of PEROXYDE OF IRON in the undissolved residuum may be easily detected, but that of MAGNESIA is more difficultly recognised; wherefore the residuum must be dissolved in muriatic acid, and the acid solution supersaturated with ammonia, which precipitates the PEROXYDE OF IRON, but leaves the greatest part of the magnesia in the solution, in which it may be detected by means of the various re-agents (page 42).

* Yet it is better, in this case, to separate the MAGNESIA from the PEROXYDE OF IRON by means of the solution of a succinate: to effect this the liquor should be saturated with ammonia, and a very slight excess of this alkali added, so that the greatest part of the PEROXYDE OF IRON remains in solution; after which the peroxyde of iron must be precipitated by means of succinate of alkali in the state of succinate of iron [persuccinate

of iron]. The filtered liquor contains then the whole of the magnesia which accompanied the PEROXYDE OF IRON.

The liquor filtered from the precipitate which was produced by supersaturating it with ammonia, and which may contain PEROXYDE OF IRON, ALUMINA, and MAGNESIA, may still contain OXYDE OF NICKEL, OXYDE OF COBALT, PROTOXYDE OF MANGANESE, and OXYDE OF ZINC. It must be treated as we have indicated before (page 656).

C. The liquor filtered from the precipitate produced by hydrosulphuret of ammonia in the solution previously supersaturated with ammonia, is first examined in order to see whether it still contains any fixed constituents; if so, it must be treated in the same manner as the corresponding liquor mentioned in the preceding chapter (page 657). On this occasion I would again remark that it is hardly necessary to look for ALKALIES, since they form with the acids in question salts which are soluble in water.

2. METHOD OF PROCEEDING TO DETECT THE ACIDS.

Some of the acids are much more difficult to detect in the combinations under consideration here than in those which are soluble in water.

The presence of CARBONIC ACID in all, and that of SULPHUR in some of these substances, is detected by the effervescence which takes place when dilute muriatic acid is poured upon a certain quantity of the compound. If the gas disengaged with effervescence is inodorous, the combination contains CARBONIC ACID only; but if the gas exhales an odour of sulphuretted hydrogen, the compound may contain simultaneously SULPHUR and CARBONIC ACID[1]. In such case it is necessary to examine whether the disengaged gas contains carbonic acid. To effect this, the combination under examination is introduced in a flask closed with a cork traversed by a small tube bent twice at right angles; dilute muriatic acid is now poured upon it and the gas disengaged is passed through a solution of *chloride of barium* or of *chloride of calcium*, to which a little ammonia has been added, or better still, perhaps, through LIME-WATER. If the current of the gas produces a white precipitate which dissolves with effervescence in muriatic acid, the combination contains CARBONIC ACID. It is necessary, however, in this experiment to shelter the liquor from the contact of the air[1].

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[1] The gas disengaged might, on the other hand, contain such a small quantity of sulphuretted hydrogen, that it could not be detected by the smell. It is well to suspend over the liquid from which the effervescence arises, a piece of paper moistened with a solution of basic acetate of lead, which will turn brown if any sulphuretted hydrogen is escaping, or else the gas may be passed ultimately through solution of acetate of lead. Metallic sulphurets may also be generally detected by the odour of sulphurous acid disengaged when roasted, or by the bleaching action of the fumes upon brazil-wood paper.—ED.

A portion of the compound is dissolved in muriatic acid, or, if oxyde of silver, suboxyde of mercury, or protoxyde of lead are present, in nitric acid; the solution is diluted with water and a solution of *chloride of barium* or of *nitrate of baryta* is added according to the acid employed. If a white precipitate is produced, the combination contains SULPHURIC ACID. If by heating a portion of the combination with nitric acid a reaction takes place with disengagement of ruddy fumes of nitrous acid and separation of sulphur, and if the liquor being diluted and filtered yields a precipitate by adding a solution of *nitrate of baryta*, the substance under examination is a metallic sulphuret. If sulphur is combined with mercury, *aqua regia* must be used instead of nitric acid; in that case CHLORINE is disengaged, and not nitrous acid. Compare what has been said in Chapter VI., (page 636).

A portion of the compound is dissolved in nitric acid, in the cold if possible, and after having diluted the solution with water, a small quantity of a solution of *nitrate of silver* is added. If a white curdy precipitate is formed, the compound is a metallic chloride.

* As SUBCHLORIDE OF MERCURY is insoluble in nitric acid, and dissolves only in *aqua regia*, it is necessary to treat a portion of the combination with solution of potash, according to the method indicated (page 641).

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[1] Because a precipitate of carbonate of lime might be produced by the absorption of the carbonic acid of the air, it is therefore advisable, in order to remove all source of error, to pour a small quantity of oil in the flask containing the lime-water, which will shield it from contact with the air.—ED.

The operator must next examine whether the combination, being treated by sulphuric acid and alcohol, gives a green flame when the alcohol is set fire to, in which case BORACIC ACID is present.

NITRIC ACID is detected by strewing a portion of the combination upon charcoal[1].

The presence of ARSENIC ACID is detected by means of the blow-pipe.

The presence of PHOSPHORIC ACID is very difficult to detect in these compounds. The substance is examined before the blowpipe, according to the directions given by Berzelius (page 270), after having ascertained that the combination contains neither arsenic, nor sulphuric acids, nor sulphur; according to Fuchs, boracic acid must likewise be absent.

The detection of this acid in the humid way is difficult.

If the bases of the combination under examination contain only such metallic oxydes as can be precipitated from the acid solution by sulphuretted hydrogen, the liquor is filtered from the precipitate produced by this re-agent, and submitted to the treatment indicated (page 268), in order to ascertain whether it contains PHOSPHORIC ACID; but the sulphuretted hydrogen must first be completely expelled by heating it. It is hardly necessary to observe, that when the operator intends using a solution of nitrate of silver as a test for detecting PHOSPHORIC ACID, the compound must be dissolved in *nitric* and not in *muriatic acid*. If PHOSPHORIC ACID be precipitated by a solution of *chloride of calcium*, or of *barium*, after having first poured an excess of ammonia in the liquor, it is always necessary to ascertain that the precipitate produced consists really of *phosphate of lime* or of *baryta*. To effect this the operator must first examine whether it contains any boracic acid, and then the presence of phosphoric acid may be ascertained by the blow-pipe.

If, on the contrary, the bases consist of metallic oxydes susceptible of being precipitated by hydrosulphuret of ammonia from the acid solution first supersaturated with ammonia;

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[1] See the other tests, page 539.

consequently, if the bases are PEROXYDE OF IRON, PROTOXYDE OF IRON, OXYDE OF NICKEL, OXYDE OF COBALT, OXYDE OF ZINC, PROTOXYDE OF MANGANESE, the liquor is first filtered from the precipitate produced by the above re-agent, and dilute muriatic acid is poured in it and the whole left to digest until all odour of sulphuretted hydrogen has vanished; it is then filtered again to separate the sulphur, and it is treated in the same manner. Of course *nitric* and not muriatic acid must be used if *nitrate of silver* is the test decided upon.

If the bases are *alumina, magnesia, lime, strontia,* and *baryta,* the detection of phosphoric acid is difficult, especially when accompanied by metallic oxydes which cannot be precipitated except by hydrosulphuret of ammonia. When, on the contrary, these earths exist alone or accompanied by metallic oxydes susceptible of being precipitated from the acid solution by sulphuretted hydrogen, PHOSPHORIC ACID may be detected in the following manner:—After having separated from the acid solution by sulphuretted hydrogen the metallic oxydes which can be precipitated by this re-agent, the liquor is to be saturated with ammonia, which will precipitate the earths when combined with phosphoric acid. If only *lime, strontia,* and *baryta* are present in the solution, their precipitation by ammonia is a proof of the presence of phosphoric acid; it is only necessary to ascertain that the precipitate contains no boracic acid and that phosphoric acid is present, [which may be done in the first case with sulphuric acid and alcohol; in the second case with the blowpipe]. If magnesia is present at the same time, it is likewise precipitated by ammonia in presence of phosphoric acid, even though the liquor contains ammoniacal salts in sufficient quantity to prevent its precipitation by ammonia, were there no phosphoric acid. *Alumina* likewise is precipitated, but its precipitation by ammonia is no proof of the presence of phosphoric acid. In order to ascertain whether it is present or not in the precipitate, the precipitate must be treated as described before (page 265).

But if these earths are accompanied in the substance under examination by *peroxyde of iron, protoxyde of iron, oxyde of nickel, oxyde of cobalt, oxyde of zinc, protoxyde of manganese,* and if other metallic oxydes, susceptible of being precipitated from the acid solution by sulphuretted hydrogen, are present at the same time, the analysis must be conducted quite in another way. The substance under examination must be dissolved in nitric acid or in muriatic acid, if the solution of nitrate of silver is not intended to be resorted to as the test for phosphoric acid, and then by means of a solution of sulphuretted hydrogen, the metallic oxydes susceptible of being precipitated thereby are thrown down. The filtered liquor is then heated until all odour of sulphuretted hydrogen has vanished; after which, dilute sulphuric acid is added, which precipitates the *baryta* and *strontia.* The *lime* may likewise be precipitated thereby if a sufficient quantity of alcohol is added[1]. The liquor is filtered to separate it from the precipitate produced, and if *lime* has been precipitated, it is heated until all the alcohol has disappeared. If then there is neither *magnesia* nor *alumina,* but metallic oxydes only susceptible of being precipitated by hydrosulphuret of ammonia, the liquor must be saturated with ammonia, the oxydes are precipitated by this re-agent, and phosphoric acid may be detected in the filtered liquor in the manner which has been described. But if *magnesia* and *alumina* are likewise present, no hydrosulphuret of ammonia is added, but an excess of solutions of pure potash is poured in, and the whole is boiled. The *protoxyde of iron, oxyde of nickel, oxyde of cobalt, protoxyde of manganese,* and *magnesia* are precipitated sometimes, it is true, with a small quantity of PHOSPHORIC ACID, but the greatest portion of that acid remains dissolved in the filtered liquor, in which it may be detected by supersaturating a small quantity of the solution with *muriatic acid,* and pouring thereon a solution of *chloride of barium,* which produces a precipitate of sulphate of baryta; if sulphuric acid has previously been added for the purpose of precipitating the *baryta,* the *strontia,* and *lime;* the precipitate is separated by filtering, after which the addition of ammonia in the filtered liquor determines a precipitate of PHOSPHATE OF BARYTA.

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[1] Sulphate of lime is very slightly soluble in water, but insoluble in alcohol.—ED.

But if *oxyde of zinc* and *alumina* are present, the phosphoric acid dissolves with these bases in pure potash. If *oxyde of zinc* alone is present, it is precipitated in the potash solution by hydrosulphuret of ammonia, and the presence of PHOSPHORIC ACID may then be ascertained in the filtered liquid. If the alkaline solution contains *alumina* alone, then the presence of PHOSPHORIC ACID may be detected in the manner described (page 265). But if the two bases exist simultaneously, hydrosulphuret of ammonia is added to the potash solution, which re-agent will precipitate the oxyde of zinc alone in the state of sulphuret of zinc; the alumina remains dissolved with the phosphoric acid if there be a sufficient quantity of potash. The hydrosulphuret of ammonia in the liquor filtered from the sulphuret of zinc produced must be decomposed, and the presence of the PHOSPHORIC ACID and *alumina* may be detected in the filtrate by the method described (page 265).

* The analysis of the oxydised combinations, which are insoluble in water, may be rendered much more easy by mixing the substance to be examined with three or four times its weight of carbonate of potash or of soda, and fusing the mixture in a platinum crucible, which for this purpose is preferable to any other. The fusion requires a stronger heat that can be produced with a spirit-lamp with circular wick, and therefore a coal or coke fire must be resorted to. The mass after fusion is left for a long time to digest in water, and the insoluble portion is collected on a filter and washed.

* This method presents the considerable advantage of procuring the acids separate from the bases in the solution. The undissolved portion consists of the bases either in the state of carbonates, as in the case of the alkaline earths, or simply in the state of metallic oxydes, or even in the metallic state, as is the case with the oxydes of silver and of gold. In the latter case a platinum crucible must not be used, because it would be attacked by the metals; a porcelain crucible should then be

employed as well as in the case of oxyde of lead, of bismuth, or of other easily reducible metallic oxydes.

* The undissolved portion is dissolved in muriatic acid. It is best to dry the precipitate a little, in order to be able to remove it as completely as possible from the filter, and to dissolve it without the paper, than to digest it with the paper in the muriatic acid. This precaution is especially necessary when nitric acid is used instead of muriatic acid, that is to say, when there are metallic oxydes which cannot be dissolved by the latter.

* The solution of the bases in muriatic acid or in nitric acid is treated precisely in the same manner as we have fully described (page 649); for as these bases are then separated from the acids, such as *phosphoric, arsenic,* and *boracic acids,* with which they formed compounds insoluble in water, their determination does not offer any difficulty.

* ALUMINA alone, if among the bases, may after the fusion of the combination with the alkaline carbonate exist in the solution of the fused mass. It must be remarked also that if oxyde of mercury existed in the substance to be examined, it must not be fused with the alkaline carbonate, since, as is well known, the mercury would volatilise.

* The aqueous solution of the mass fused with the alkaline carbonate contains the acids of the combination, namely, SULPHURIC, PHOSPHORIC, ARSENIC, BORACIC ACIDS, and CHLORINE. The acids are united with the alkali, and the chlorine with the metal of that alkali. Moreover the liquor contains the excess of the alkaline carbonate. It is very easy to ascertain the presence or absence of these acids, which is done by following the method indicated (page 662). Yet it must not be forgotten that the solution contains some alkaline carbonate in the free state.

* If the substance under examination contains any *alumina,* as I have already remarked before, it has passed into the alkaline solution of the acids. By gradually saturating this solution with an acid, a precipitate is produced, which re-dissolves in an excess of the acid employed. If *ammonia* is now added to the

acid liquor, the alumina is precipitated (combined with the phosphoric or arsenic acids, if these acids existed in the compound).

* The presence of NITRIC ACID and that of CARBONIC ACID cannot be detected when this method of analysis is followed. The first, because it is decomposed by fusion with the alkaline carbonate; the second, because an excess of alkaline carbonate has been employed to effect the fusion. The presence of these two acids must therefore be sought for in other portions of the substance.

If that substance contains METALLIC SULPHURETS insoluble in water, it may be treated in a similar manner—that is to say, it should be reduced into fine powder, mixed with double its weight of carbonate of potash or of soda, and four times its weight of nitrate of potash or of soda. The mixture is fused in a small porcelain crucible, and as the addition of the nitrate of alkali renders the mass easy of fusion, the whole is exposed to the flame of a spirit-lamp with circular wick. When the melted mass is afterwards treated by water, the sulphate of alkali produced and the excess of alkaline carbonate are dissolved, accompanied perhaps by a little nitrate or nitrite, and leave the metals in the state of oxydes. This method is sometimes advantageous in case of metallic sulphurets, but is not preferable to the ordinary method of treating them by nitric acid or aqua regia. It is suitable more especially when sulphuret of lead is among the number of the sulphurets in the compound.

* ALLOYS must always be treated in the usual way, that is to say, by nitric acid or aqua regia. The metallic arseniurets are the only ones, for the qualitative analysis of which the fusion with a mixture of carbonate and of nitrate of alkali is really advantageous. When the fused mass is treated by water, it dissolves not only the carbonate but the nitrate, nitrite and arseniate of alkali also. The metals remain in the state of oxydes, quite freed from arsenic acid, and, therefore, may be easily examined.

CHAPTER X.

COURSE OF THE QUALITATIVE ANALYSIS OF MIXED COMPOUNDS WHICH ARE TOTALLY INSOLUBLE, OR NEARLY SO, IN WATER AND IN ACIDS, AND THE CONSTITUENTS OF WHICH ARE AMONG THOSE OF THE LIST (Page 622.)

If, after first treating the substance under examination by water, then by an acid, there still remains an insoluble precipitate, it can consist only of the substances mentioned in Chapter VII. (page 645), namely, SULPHATE OF BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, SULPHATE OF LEAD, and CHLORIDE OF SILVER.

The combination is fused with about twice or three times its weight of dry carbonate of soda[1]. If the operator knows that it contains no *chloride of silver* the operation may be performed in a platinum crucible; but if the substance contains *sulphate of lead,* it is necessary to manage the fusion with great care, and only expose the crucible to a low red heat. In most cases, it is not so advantageous to use a porcelain crucible for the reasons mentioned (page 675). Yet a porcelain crucible should always be used when *chloride of silver* is present[2]. When the fused mass has cooled, water is poured upon it and left till it softens; it is then digested in a larger quantity of water still, and it is filtered in order to separate the insoluble portion. The clear liquor is now saturated with nitric acid. The presence of SULPHURIC ACID is detected by pouring a solution of nitrate of baryta in a portion of that liquor; and that of CHLORIDE OF SILVER by means of a solution of nitrate of silver, which produces then a precipitate due to the presence of chloride of sodium.

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[1] The substance should be first reduced to a fine powder, and rubbed in a glazed porcelain mortar with the quantity of alkaline carbonate decided upon, so as to mix the mass thoroughly, after which it is transferred to the crucible, in which it is intended to fuse it. When this is done the mass must not be exposed to too strong a heat at first, because the carbonic acid which disengages would cause the mass to swell up and boil over.—Ed.

[2] When a porcelain crucible is used, silica is always found among the products of the fused mass which are soluble in water, and which proceeds from the substance of the crucible, which has been acted upon by the alkaline carbonate.—Ed.

The residuum can consist only of CARBONATES OF BARYTA, of STRONTIA, of LIME, and of LEAD. It may also contain *metallic silver,* if chloride of silver was present in the compound. The silver is in the form of a metallic bead at the bottom of the crucible, provided a very strong heat has been employed to effect the fusion; if the heat has been less powerful so that the whole has not fused in a regular manner, the silver remains in the state of extreme division when the mass is treated by water. The residuum is dissolved in nitric acid; but if neither silver nor carbonate of lead exist, it is better to employ muriatic acid. Dilute muriatic acid is poured in a small portion of the solution for the purpose of ascertaining whether it contains oxyde of silver; if so, the chloride of silver produced must be separated by filtering, and ammonia is added to the filtered liquor. If a white precipitate is produced, it indicates the presence of PROTOXYDE OF LEAD.

If the combination contains OXYDE OF SILVER and OXYDE OF LEAD, the greatest part of the solution must be treated by solution of sulphuretted hydrogen in order to precipitate these two bases. The liquor filtered from the precipitate thus produced, and which may still contain LIME, STRONTIA, and BARYTA, is mixed with HYDROFLUOSILICIC ACID. If, after a time, a precipitate is produced, it indicates the presence of baryta. The liquor is separated from this precipitate, and if a solution of sulphate of potash, or of very dilute sulphuric acid, produces an immediate precipitate, STRONTIA is present, either alone or accompanied by LIME. In order to ascertain this, the sulphate of strontia (if any has been produced) is collected on a filter, and the liquor is saturated by ammonia. If a solution of an oxalate, poured drop by drop in the liquor, determines a white precipitate, it is a proof of the presence of LIME.

Several acid PHOSPHATES, and certain acid ARSENIATES, also some other combinations, become insoluble in water and the dilute acids, after having been exposed to a strong red heat [1]. The operator, however, may very easily, by means of the blowpipe, ascertain the presence of ARSENIC ACID, and of several METALLIC OXYDES in these salts; but that of PHOSPHORIC ACID is not quite so easily detected before the blow-pipe. The substance must be pulverised, and the powder put in a small porcelain capsula, concentrated sulphuric acid poured upon it, and the whole heated even to ebullition for some time. The insoluble substance is thereby decomposed, and water being added, it dissolves therein. When the base is not of such a nature as to form an insoluble, or sparingly soluble, compound by uniting with sulphuric acid, as for example, oxyde of lead, lime, strontia, baryta, these four bases are distinguished from each other in the manner which has been just described; but the solution is examined by the method which we have indicated in Chapter IX. of this part (page 675).

These combinations may be also qualitatively analysed by fusing them with carbonate of potash or of soda, and then the course mentioned in the preceding chapter (page 675) should be followed.

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[1] Such is the case amongst others with *peroxyde of tin*, and *peroxyde of iron*. In the case of peroxyde of tin, carbonate of potash should be replaced by caustic potash and a silver crucible used.—ED.

CHAPTER XI.

COURSE OF THE QUALITATIVE ANALYSIS OF SUBSTANCES WHICH MAY CONTAIN ALL THE INORGANIC CONSTITUENTS HITHERTO KNOWN.

* When the object in view is the qualitative analysis of an unknown substance of whatever kind, it is suitable to follow a process analogous to that which has been developed in the preceding chapters. The first step is to ascertain whether the combination is soluble or insoluble in water, then a portion of it is devoted to the examination of the bases, and another to that of the acids. We have seen in the preceding chapters, that, in the course of the operations necessary for the detection of the bases, very often several acids are at the time discovered.

It is impossible with respect to the analysis of unknown substances, which may contain the most various inorganic constituents, to enter into particulars as precise and circumstantial as for those the number of which is limited; wherefore, I intend only to show here how, in such an analysis, the various constituent bodies may be divided into certain groups, the examination of each of which no longer presents any difficulty.

* I have already said that the presence of certain bodies excludes that of other substances in the compound under analytical research. It is unnecessary to mention again here, those which cannot be met with simultaneously in a similar compound. With respect to the behaviour of the various bases

towards the re-agents, that which is important to be borne in mind is this; namely: what are the acids which form soluble or insoluble combinations. I have also stated, in speaking of each acid, what are the bases which produce soluble or insoluble salts. I have only one thing more to add, namely; that amongst the acids and the bases to the presence of which I have paid little or no attention in the preceding chapters, there are several which possess a very reducing action upon a great number of metallic oxydes the metals of which have not much affinity for oxygen. For example, SULPHUROUS, HYPOSULPHUROUS, PHOSPHOROUS, HYPOPHOSPHOROUS, OXALIC, STANNOUS ACIDS, PROTOCHLORIDE OF TIN, PROTOXYDE OF IRON, PROTOCHLORIDE OF IRON, cannot co-exist in presence of the oxydes or chlorides of a great number of metals called noble.

1. QUALITATIVE ANALYSIS OF SUBSTANCES SOLUBLE IN WATER.

* A.—DETECTION OF THE BASES.

The modus operandi described in Chapters V. and VI., may serve as models.

(a). The concentrated solution of the compound is first rendered acid by adding *muriatic acid* thereto, or, in some cases already mentioned before (page 625), dilute nitric acid.

* When muriatic acid having been added to a concentrated solution of the compound, the operator remarks that by heating the whole a well-defined odour of *chlorine gas* is evolved, it is a proof that the aqueous solution may contain PEROXYDE OF MANGANESE, PEROXYDE OF CERIUM, MANGANIC ACID, VANADIC ACID, CHROMIC ACID, OR SELENIC ACID. If the action of the heat is prolonged until the evolution of chlorine has ceased, the above constituents are converted, at least partially, into PROTOXYDE OF MANGANESE, PROTOXYDE OF CERIUM, VANADOUS ACID, OXYDE OF CHROMIUM, SELENIOUS ACID, and may afterwards be recognised as such in the solution. The CHLORATES and the combinations of the CHLORITES with the metallic chlorides, may likewise disengage chlorine, when treated

by muriatic acid (pages 244, 251), which observation applies also to the BROMATES and IODATES.

* By adding an acid to the solution of the substance, a precipitate may in some cases be formed, which is due to the acids which are combined with the bases being set at liberty, and precipitated when they are insoluble in water. Ordinarily the acid which is thus precipitated re-dissolves in an excess of muriatic or of nitric acid, yet this phenomenon does not take place with TANTALIC ACID (page 291), TUNGSTIC ACID (page 310), TITANIC ACID, which remain insoluble in the liquor containing the excess of muriatic acid. It is easy to recognise by means of the blow-pipe the TITANIC and TUNGSTIC acids which are thus liberated. TUNGSTIC ACID may likewise be distinguished from TITANIC ACID and from TANTALIC ACID by its great solubility in hydrosulphuret of ammonia. SILICIC ACID is also separated from an acid solution to which another acid is added, in an excess of which it remains insoluble. It may likewise be very easily distinguished before the blow-pipe.

* Muriatic acid mixed with the solutions of the SULPHOSALTS soluble in water, decomposes the sulphobase which then remains dissolved, whilst a metallic sulphuret insoluble in water is separated, and may be subsequently examined. This decomposition is generally accompanied by a disengagement of sulphuretted hydrogen.

* If, however, the addition of muriatic acid or of nitric acid to the aqueous solution of the combination under examination does not determine any of these changes, a solution, or current of sulphuretted hydrogen is passed through the acid liquor. In this way not only are the oxydes mentioned before (page 626), namely, OXYDE OF CADMIUM, PROTOX OF LEAD, OXYDE OF BISMUTH, PROTOXYDE OF COPPER, OXYDE OF SILVER, SUBOXYDE OF MERCURY, PROTOXYDE OF MERCURY, OXYDE OF GOLD, PROTOXYDE OF TIN, PEROXYDE OF TIN, and OXYDE OF ANTIMONY, but several others, namely:—OXYDE OF RHODIUM, OXYDE OF IRIDIUM, OXYDE OF OSMIUM, OSMIC ACID, PROTOXYDE OF PALLADIUM, OXYDE OF PLATINUM, ANTIMONIOUS ACID, ANTIMONIC ACID, the OXYDES

OF MOLYBDENUM, MOLYBDIC ACID, TELLURIOUS ACID, ARSENIOUS ACID, ARSENIC ACID, and SELENIOUS ACID, are precipitated in the state of metallic sulphurets. It is hardly necessary to observe that the CHLORIDES, BROMIDES, IODIDES, and FLUORIDES of these metals, when they exist in the solutions instead of the oxydes, are likewise precipitated by sulphuretted hydrogen. Some of the metallic sulphurets thus produced do not separate except after a long time, and several, even not until after heat is applied to the liquor, a circumstance which has been taken into consideration, and alluded to in the first part of this volume, and which must be especially borne in mind.

* Some oxydes are not precipitated from their acid solutions in the state of metallic sulphuret by sulphuretted hydrogen, they however decompose this re-agent, the result of which is, that after heating the liquor, *sulphur* is precipitated in the shape of a milky precipitate which is difficult to filter. To this class the following substances belong :—SESQUIOXYDE OF MANGANESE, the acids of MANGANESE and CHROMIC ACID, when they have not been previously decomposed by muriatic acid ; PEROXYDE OF IRON, HYPOSULPHURIC ACID, SULPHUROUS ACID, CHLORIC ACID, BROMIC ACID, and IODIC ACID, when the solutions of the salts of these acids have been previously decomposed by an acid. If the combination under examination does not contain any metallic oxydes susceptible of being precipitated in the state of metallic sulphurets by sulphuretted hydrogen, the separation of sulphur demonstrates the presence of one or of several of these immediate substances. It is very easy to distinguish the sulphur liberated from a metallic sulphuret; but it is impossible to recognise the liberation of sulphur when a metallic sulphuret is at the same time precipitated.

* The metallic sulphurets precipitated by sulphuretted hydrogen are next treated by hydrosulphuret of ammonia in the manner indicated (page 650), and the solution thus obtained must be treated as described there also. Among the metallic sulphurets precipitated, *hydrosulphuret of ammonia* dissolves those, the oxydes of which have been indicated (page 473);

consequently the sulphurets of PLATINUM, of IRIDIUM, of GOLD, of TIN, of ANTIMONY, of MOLYBDENUM, of TELLURIUM, of SELENIUM, and of ARSENIC, TUNGSTIC ACID, VANADOUS ACID, and VANADIC ACID, which cannot be precipitated in the state of metallic sulphurets from acid solutions, dissolve also in the state of oxydes in hydrosulphuret of ammonia, and an acid may then precipitate them in the state of sulphurets from that solution.

* The presence of PLATINUM is easily detected in the solution of the substance under examination, because when concentrated, a solution of *chloride of potassium* or of *muriate of ammonia* also concentrated, produces a yellow precipitate (page 149). If the solution of the substance under examination be very dilute, it should first be concentrated before pouring in the solution of chloride of potassium, or of muriate of ammonia.

* The presence of IRIDIUM may be detected by treating a portion of the solution of the substance under examination in the same manner as for platinum. Its very concentrated solution is precipitated by chloride of potassium, or muriate of ammonia, especially when the combination has been dissolved in alcohol; yet the precipitation generally does not take place except after a long time. The double salt formed is black, but if the liquor contains platinum at the same time, the precipitate has a reddish tinge.

* The presence of MOLYBDENUM is detected by treating a portion of the compound under examination in the dry state before the blow-pipe (page 188), yet it must not contain at the same time any substance capable of preventing the manifestation of the phenomena produced by the blow-pipe. In order to remove this obstacle, it is therefore better to treat before the blow-pipe the precipitate which has been produced by muriatic acid in the solution of the metallic sulphurets in hydrosulphuret of ammonia.

* Sometimes the milkiness produced in the solution by addition of water, when the acid has not been used in too large quantities, is sufficient to indicate the presence of TELLURIUM;

but a conclusive proof is the reaction which the liquor exhibits with the alkalies (page 228), and by the behaviour of the compound before the blow-pipe. Yet it is especially in the liquor obtained by treating with nitric acid or aqua regia, the metallic sulphurets which have been dissolved by hydrosulphuret of ammonia, that the presence of TELLURIOUS ACID, must be sought for, and not immediately in the solution of the substance under examination, because the analyst very often runs the risk of failing to perceive it in this solution when accompanied by several metallic oxydes playing the part of bases.

* In many cases the presence of SELENIUM may be immediately detected by the blow-pipe (page 221), yet SELENIUM may be detected in the solution, either in the state of SELENIC ACID, or of SELENIOUS ACID, by means of the re-agents mentioned (page 219 to 221). It is especially easy to detect it by treatment with sulphurous acid, after having converted selenic acid (if it exists therein) into selenious acid.

* The presence of ARSENIC, which may be contained in the aqueous solution in the state of arsenic acid or of arsenious acid is, in such a case, very easily detected by means of the blow-pipe. In order to ascertain whether the metal is in the state of arsenic acid or of arsenious acid, the experiments described (page 346) must be resorted to.

* I have said (page 651), how the operator must proceed to detect the other substances, GOLD, TIN, ANTIMONY.

The metallic sulphurets which are not dissolved by hydrosulphuret of ammonia, and the corresponding oxydes of which have been indicated, (page 472), are the sulphurets of CADMIUM, of LEAD, of BISMUTH, of COPPER, of SILVER, of MERCURY, of PALLADIUM, of RHODIUM, and of OSMIUM. I have shown, (page 472), how the presence of the first six of these metals can be detected. That of PALLADIUM is detected in the solution by pouring a solution of *cyanide of mercury* (page 154), which method at most can in a small number of cases lead to confound this metal with platinum (page 150). That of RHODIUM is detected in the dry combination by fusing it with bicarbonate of potash (page 158). OSMIUM is very easily recognised by the characteristic odour which its solution exhales when boiled with nitric acid (page 167).

(b). After having treated the acidified solution of the substance under examination by sulphuretted hydrogen, the liquor filtered from the metallic sulphurets which have been thereby precipitated, is saturated by ammonia and decomposed by hydrosulphuret of ammonia. It is then treated absolutely, as has been prescribed for liquor B in Chapter VIII., (page 654), and all the precautions there recommended must be observed. By following that process, the combinations of sulphur with the metals of the oxydes mentioned (page 471), are precipitated, consequently the sulphurets of MANGANESE, of IRON, of ZINC, of COBALT, of NICKEL, and of URANIUM. I have already said, in Chapter VIII., (page 654), what the operator must do in order to detect the first five of these metals. As to the presence of URANIUM, it is detected by treating the solution of these metallic sulphurets in nitric acid or aqua regia by carbonate of ammonia, which will dissolve the peroxyde of uranium, producing a yellowish liquor; or by *ammonia,* which will produce a yellow precipitate; peroxyde of uranium being insoluble in ammonia (page 108), by which means it is distinguished from the combinations of *nickel, cobalt, manganese,* and *zinc,* which are all soluble both in carbonate of ammonia and in pure ammonia.

* Besides the metallic sulphurets first mentioned, the ammonia used for saturating the liquor, or if neutral, the addition of hydrosulphuret of ammonia, may further have precipitated ALUMINA, GLUCINA, THORINA, YTTRIA, PROTOXYDE OF CERIUM, ZIRCONIA, TITANIC ACID, OXYDE OF CHROMIUM, TANTALIC ACID, as we have said, (page 472). I have also shown, (page 655), the manner of detecting the presence of ALUMINA in this precipitate. The precipitate produced by ammonia and hydrosulphuret of ammonia is dissolved in nitric acid, and an excess of pure POTASH is added to the solution after having first ascertained that all the sulphuretted hydrogen has been driven off or decomposed. Among the substances precipitated in the first instance this

re-agent will dissolve only OXYDE OF ZINC, ALUMINA, and GLUCINA. Muriate of ammonia poured in the potash solution precipitates only alumina and glucina, and the presence of the OXYDE OF ZINC is then next very easily detected in the filtered liquor by hydrosulphuret of ammonia. A solution of *carbonate of ammonia* added in excess, or poured upon the precipitate [produced by muriate of ammonia] easily distinguishes ALUMINA from GLUCINA, and may even be employed to separate them if they exist simultaneously (page 50). But when the ALUMINA thus obtained, being treated before the blow-pipe, gives with solution of nitrate of cobalt a pure blue colour (page 47), it is not necessary to look for GLUCINA[1]. The residuum which has remained insoluble in potash is digested with a solution of *carbonate of ammonia,* which principally dissolves THORINA, YTTRIA, PROTOXYDE OF CERIUM, and ZIRCONIA; yet in order to effect this, very large quantities of the alkaline carbonate are required, and it is sometimes difficult to distinguish these substances, especially when they exist only in small quantity in the solution: this may, however, be successfully effected by bearing in mind what I have said in the first part of this volume in reference to their behaviour towards re-agents. The presence of TITANIC ACID, which, however, can scarcely ever be met with in compounds which are soluble in water, is recognised, especially if oxyde of cobalt and protoxyde of manganese are absent in the undissolved residuum, either by means of the blow-pipe (page 299), or by means of a bar of metallic zinc (page 296). Its presence may already be suspected when by boiling the dissolved compound after the addition of an acid, as we have said above, a precipitate which it is difficult to separate by filtering is formed (page 294). Neither can TANTALIC ACID exist in the solution rendered acid, since it is precipitated by acids from its solution in potash, as we have remarked before. The presence of OXYDE OF CHROMIUM is very easily detected before the blow-pipe, even though the compound contains only very small quantities of this oxyde.

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[1] Because if the glucina was present, the colour instead of being of a pure blue would have a greyish or black tinge.—ED.

The best way, therefore, is to test the precipitate formed by hydrosulphuret of ammonia before the blow-pipe in order to ascertain whether chromium is present (page 198).

* It is hardly possible that the precipitate obtained by ammonia and hydrosulphuret of ammonia can contain other bases than those which we have just examined, for the re-agents of which we have spoken precipitate the alkaline earths from an acid solution only when united with an acid, with which they form compounds, which are insoluble in water. When these alkaline earths are combined with a great excess of such an acid, their acid salts may thus be soluble in water, but such a solution must then be treated exactly as the acid solutions of substances which are insoluble in water.

* c. The liquor filtered from the precipitate produced by hydrosulphuret of ammonia may further contain the following bases :—MAGNESIA, LIME, STRONTIA, BARYTA, LITHIA, SODA, POTASH.—If the combination contains AMMONIA, this substance exists also in the liquor, but I have already said, (page 662), that a fresh sample of the dissolved combination must be taken in order to detect this alkali.

* The liquor is treated as we have said, (page 657.) I have also shown there how the above-named bases, except LITHIA, can be recognised. With respect to LITHIA, if in small quantity, and especially if MAGNESIA, POTASH, and SODA exist simultaneously with it, its presence may be easily overlooked: it has often occurred also that small quantities of lithia have been mistaken for *magnesia*. After having separated the *lime*, *strontia*, and *baryta* by carbonate of ammonia in the manner mentioned before (page 657), the precipitate obtained cannot contain any LITHIA if, before precipitating by carbonate of ammonia, the liquor was not too concentrated. To a portion of the solution separated from the earthy carbonates by filtering, a solution of *phosphate of soda* is added; if even, after some time, this re-agent produces no precipitate, LITHIA is absent, and if a precipitate is produced, it may be owing to the presence of LITHIA or of MAGNESIA or both. In order to ascertain this,

another portion of the liquor filtered from the earthy carbonates is evaporated to dryness, and the dry residuum is ignited in order to expel the ammoniacal salts. The ignited mass, if it contain MAGNESIA, dissolves completely in water only if the bases are combined with sulphuric acid. If this is not the case, a little sulphuric acid is added after the ignition, the excess of which must be completely expelled by slightly igniting the mass which is next to be dissolved in a small quantity of water, and to this solution one of pure potash is added, which precipitates MAGNESIA from the neutral liquor, but not LITHIA. If the solution of potash determines no precipitate, LITHIA alone was present. If, on the contrary, it produces a precipitate, the presence or absence of magnesia must be rendered conclusive by testing the liquor filtered from the magnesia by a phosphate of alkali.

* It is more difficult, in presence of *lithia* and *magnesia*, to decide at the same time whether POTASH and SODA are present or absent. If the combination contains LITHIA alone, without *magnesia*, a portion of the liquor filtered from the earthy carbonates is evaporated to dryness, and the residuum is ignited in order to expel the ammoniacal salts. A portion of this residuum is then dissolved in the least possible quantity of water, or in alcohol; if soluble therein, and the solution is tested for POTASH by *chloride of platinum*, SODA is also sought for in the residuum of the evaporation of part of the solution by means of the blow-pipe (page 13)[1].

* If, however, MAGNESIA is still found in the liquor filtered from the earthy carbonates, it is separated from the alkalies, that is to say, from *lithia*, *soda*, and *potash*, whether they exist all or only some of them, in the manner described (pages 659, 660)

for the purpose of separating *magnesia* from *potash* and from *soda*. The best and safest method, however, is to convert these bases into sulphates, if not already in that state, and to separate them by means of a solution of acetate of baryta, according to what has been said (page 662); though even then it is really somewhat difficult to separate by means of water only, the *magnesia* from the *carbonate of lithia* obtained, and which is very sparingly soluble. If the alkalies be in the state of carbonates their bases are easily detected.

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[1] The presence of a small quantity of chloride of lithium may be easily distinguished in chloride of sodium by fusing the mixture before the blow-pipe on a platinum wire, plunging the fused mixture into tallow, and lighting it after having withdrawn the wire. If the lithium be not in too small quantity, the reddish sparkling which is characteristic of lithium may be observed at the edge of the flame. This sparkling, says Berzelius, is very fine with 1 per 100 of lithium, and is still visible with 0·1 per cent. This process was discovered by M. Stein.—Ed.

B. DETECTION OF THE ACIDS.

* WE intend here, whilst treating of the acids, to speak at the same time of such of the simple substances which by uniting with the metals form compounds which are analogous to salts, for example, *iodine, bromine, fluorine*, &c., as we have already done in the preceding chapters.

* The presence of certain acids which, in the solution of their salts, are susceptible of being reduced by muriatic acid with the help of heat into a lower degree of oxydisation may, as we have already said before, be presumed from the odour of chlorine which is disengaged during the operation. To this class of acids the following belong:—SELENIC ACID, which is thereby converted into *selenious acid* (page 220); CHROMIC ACID, thereby converted into *oxyde of chromium*, a transformation which is accomplished very easily by adding some alcohol to the solution mixed with muriatic acid (page 319); and the ACIDS OF MANGANESE, which are reduced into *protoxyde of manganese* (page 323).

* I have already said before that some acids are precipitated from their solutions by muriatic acid when they are insoluble in water, and that an excess of acid does not re-dissolve them. These acids have been enumerated (page 684).

* Neither is it necessary here to pay any regard to the acids which are converted by sulphuretted hydrogen into metallic sulphurets, and which are precipitated in that state from the

acid solution, for we have already spoken of them in indicating the course of qualitative analysis for the detection of the bases.

* A. The first thing to be done when an unknown substance is to be analysed, with a view to ascertain what *acids* it contains, is to examine whether any VOLATILE ACIDS are present. To effect this it is first reduced to powder, a portion of the powder is put in a dry glass, and concentrated sulphuric acid is poured upon it, and if a reaction is not immediately manifested, the whole is very gently heated. The volatile acids are thereby expelled, and their odour alone is sufficient to distinguish them; but they are more clearly recognised still by the white clouds which are produced when a glass rod, moistened with ammonia, is plunged in the glass, taking care not to touch the mass with it. The acids which are thus volatilised by concentrated sulphuric acid in a decomposed or an undecomposed state are: SULPHUROUS ACID, immediately recognised by its well-known pungent odour (page 208); HYPOSULPHUROUS and HYPOSULPHURIC ACIDS, both of which disengage sulphurous acid when decomposed by an acid (pages 206, 215); NITRIC ACID, the salts of which yield colourless vapours when treated in the cold by sulphuric acid (page 235), but which is easily distinguished by other reactions from the salts produced by other volatile acids; NITROUS ACID, the salts of which emit ruddy fumes when so treated (page 239); CHLORIC ACID, the salts of which disengage chlorous acid when treated by sulphuric acid (page 246); BROMIC ACID, the salts of which when treated by sulphuric acid evolve gaseous bromine, easily recognised by its characteristic odour, and oxygen gas (page 255); CARBONIC ACID, the salts of which either in the solid state or in dilute solutions disengage carbonic acid with effervescence, not only when treated by sulphuric acid, but also by all the acids soluble in water (page 383); OXALIC ACID, which either in the aqueous state or combined with bases in the state of salts is decomposed with effervescence by sulphuric acid into carbonic acid and carbonic oxyde (page 389)

* Concentrated SULPHURIC ACID disengages also muriatic acid from most, not from all, the METALLIC CHLORIDES (page 422);

gaseous bromine, sulphurous and hydrobromic acids, from nearly all the METALLIC BROMIDES, which substances may be recognised by their odour or colour (page 429); gaseous iodine of a purple colour and sulphurous acid from almost all the METALLIC IODIDES (page 434); HYDROFLUORIC ACID, which is distinguished from all other acids by its action upon glass, from the metallic fluorides (page 438); fluosilicic, and hydrofluoric acid gases from the METALLIC SILICIFLUORIDES (page 445); fluoboric gas and hydrofluoric acid from the metallic BOROFLUORIDES (page 447). The METALLIC SULPHURETS treated by concentrated sulphuric acid disengage, some of them sulphuretted hydrogen, others sulphurous acid.

* It is easy to recognise a volatile acid which has been disengaged from its salts by sulphuric acid, whether it has undergone decomposition or not previous to its volatilisation. In most cases the odour or the colour of the gas disengaged is sufficient to decide what acid may be contained in the combination. In order to acquire conclusive proofs upon this subject, the combination must be treated by the test which may produce distinctive and characteristic reactions with the acid in question, and which re-agents have been indicated in the first part of this volume. When a combination contains at the same time several volatile acids, they may easily be distinguished from each other.

* The SULPHITES decomposed by means of the acids, disengage the characteristic odour of sulphurous acid only when they are not mixed with such salts as give, when decomposed by sulphuric acid, an acid or some other substance which easily abandons its oxygen, for example, with *nitrates, chlorates,* &c. In the same manner, when a SULPHITE is mixed with a metallic sulphuret which evolves sulphuretted hydrogen when treated by acids, this gas destroys the liberated sulphurous acid (page 450); in such cases the metallic sulphuret can no more be distinguished by the odour of sulphuretted hydrogen than the sulphite by the odour of sulphurous acid, unless there be an excess of one or the other of these gases. The SULPHITES which are decomposed

by sulphuric acid can be distinguished by the odour of the sulphurous acid disengaged only when mixed with carbonates or oxalates, with metallic chlorides or fluorides, or with salts containing fixed acids.

* The same is the case with the HYPOSULPHATES and HYPOSULPHITES. When a HYPOSULPHITE is accompanied by a metallic sulphuret soluble in water, as is the case when sulphur has been fused with an alkaline hydrate, or when it has been boiled with the solution of an alkali, the presence of that salt can be recognised only by mixing the solution with an excess of a neutral salt of zinc. The soluble metallic sulphuret precipitates sulphuret of zinc, whilst the excess of the salt of zinc and the hyposulphite remains in solution. If muriatic acid is now poured in the filtered liquor, the presence of the hyposulphite is detected by the odour of the sulphurous acid disengaged, and the precipitate of sulphur formed.

* The NITRITES or NITRATES, even when mixed with several other salts, are recognised by the property which they have of fusing upon ignited coals[1]. The nitrates contained in a mixture may be recognised also because they disengage ruddy vapours of nitrous acid, when treated by copper filings and sulphuric acid (page 235). Their presence in a concentrated solution is easily detected, even in presence of other salts, by means of a protosalt of iron and sulphuric acid (page 233), but the bleaching of the solution of indigo is not always a trustworthy test,

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[1] The deflagration, observes Berzelius, takes place only with the fusible nitrates; those which are not so must be perfectly dried, and then heated to redness in a glass tube closed at one end, when ruddy fumes will soon be observed rising in the glass. On the other hand, as several other substances behave in the same manner when thrown upon red-hot charcoal, it is therefore absolutely necessary to test the compound by the other methods which have been described. M. A. Vogel has indicated the following method to distinguish the *nitrates* from the *chlorates*, in very dilute solutions; it is as follows:—Add acetic acid to the solution in sufficient quantity to render it acid, and pour into it a few drops of tincture of litmus. If there be any nitric acid in the solution the blue colour is simply changed into red, but it is entirely bleached if a chlorate be present. By this means one part of chlorate may be detected in five hundred parts of water. Berzelius adds, that the liquid must not contain less than $\frac{1}{84}$ of its weight of chlorate of potash, else the reaction cannot be well observed.—ED.

because several other salts, for example the *chlorites*, have a similar action.

* The presence of the CHLORATES and BROMATES, even when mixed with several other salts, is easily recognised, because, when exposed in the dry state, in a small retort, to a moderate heat, they disengage oxygen (pages 246, 255), which takes place at a temperature less elevated than that required by the nitrates to produce the same phenomenon. The *iodates* behave in the same manner (pages 257, 259).

* The CARBONATES are more easily recognised than almost any other salt, even when mixed with many other salts, by the inodorous gas which they disengage with effervescence when an acid is poured in even moderately dilute solutions. I have already shown (page 662) how the presence of carbonic acid can be detected when the salt is accompanied by a metallic sulphuret which, when decomposed by the acids, disengages sulphuretted hydrogen with effervescence.

* The presence of the OXALATES is indicated in solution by their characteristic behaviour with solution of sulphate of lime (page 387), even in presence of other salts, for of all the inorganic acids which sulphuric acid displaces, there is not one which presents this reaction.

* The MANGANATES and HYPERMANGANATES are so easily recognised by most of their properties, that their presence is not difficult to detect, even when accompanied by other salts.

* The METALLIC CHLORIDES are easily recognised in solutions, even when they contain, besides many other salts, other acids also, by their behaviour towards a solution of oxyde of silver (page 420). The insolubility of the precipitate thus produced in nitric acid is a more characteristic test of the presence of chloride of silver than the solubility of that same precipitate in ammonia, because though chloride of silver is very soluble in volatile alkali yet this re-agent often produces in the solution a white precipitate of other substances, which may lead an inexperienced chemist into error by making it appear that the chloride of silver is not soluble in ammonia. This is the case, for example, when the solution

contains perchloride of mercury. *Bromide, iodide, bromate,* and *iodate* of silver, like the chloride of this metal, are insoluble in dilute nitric acid.

* It is true that the metallic BROMIDES and IODIDES, and the BROMATES, are easily detected in solution, yet the operator is exposed in presence of these substances, to overlook that of a metallic chloride. I have already said (pages 429, 435) how a soluble metallic chloride can be recognised when it exists in a combination simultaneously with a soluble bromide or iodide.

* When METALLIC BROMIDES OR CHLORIDES are mixed with some salts containing a metallic acid, concentrated sulphuric acid may disengage from such mixtures volatile combinations of chloride, which in some cases have a characteristic odour, for example, when other combinations are accompanied by chromates (page 423).

* The presence of the METALLIC FLUORIDES is very easily detected in the ordinary way, even though these compounds be accompanied by all the other salts (page 437).

* The presence of the METALLIC FLUORIDES is detected in the metallic silicofluorides by the means described before, and FLUORIDE OF SILICIUM is recognised by the precipitate of silicic acid which the alkalies determine in the solution.

* The METALLIC BOROFLUORIDES are detected in all kinds of combinations by decomposing them by means of sulphuric acid, in consequence of which they attack glass, and because, when they are mixed afterwards with alcohol, they impart a green colour to the flame.

* I have shown (page 662) how the presence of METALLIC SULPHURETS can be detected in mixed compounds.

B. If sulphuric acid has failed in disengaging from the combinations any volatile acid, either in a decomposed or undecomposed state, the combination may contain IODIC ACID, PHOSPHORIC ACID, PHOSPHOROUS ACID, HYPOPHOSPHOROUS ACID, BORACIC ACID, SILICIC ACID, and several other acids, for the detection of which, means have already been indicated whilst speaking of the detection of the bases. If SELENIC ACID is present, the analyst's attention is arrested at this part of the analysis, because the combination disengages chlorine when heated with muriatic acid, the selenic acid being at the same time converted into selenious acid, which may then be precipitated by sulphuretted hydrogen in the state of sulphuret of selenium.

* The IODATES are recognised because they are reduced by the re-agents into metallic iodides, or into iodine, which may then be easily detected by starch.

* The PHOSPHITES and HYPOPHOSPHITES are easily recognised, because they produce a precipitate of subchloride of mercury when poured in a solution of perchloride of mercury, to which a little muriatic acid is added. Yet in order to obtain this reaction it is necessary that an excess of perchloride of mercury be employed, otherwise it is metallic mercury which is precipitated from the solution (pages 273, 277). But these salts behave in such a characteristic manner when exposed to a red heat that they cannot be confounded with any other. When HYPOPHOSPHITES are heated with concentrated sulphuric acid they are decomposed, sulphurous acid is disengaged, and they are converted into phosphoric acid.

* SILICIC ACID is completely separated from its alkaline solutions by evaporating to dryness the liquor saturated with muriatic acid, and treating the residuum by water (page 286).

* I have already shown (page 662) what is to be done for the purpose of detecting PHOSPHORIC and BORACIC ACIDS in complicated compounds.

2. ANALYSIS OF THE SUBSTANCES WHICH ARE INSOLUBLE IN WATER.

* IF the substance is insoluble in water it must be dissolved in *hydrochloric acid*, or sometimes either in *nitric acid* or in *aqua regia*. Treated by hot muriatic acid, several insoluble peroxydes disengage chlorine; this is the case with the CHROMATES, SELENIATES, VANADATES, SESQUIOXYDE OF CERIUM, SESQUIOXYDE OF MANGANESE, and PEROXYDE OF MANGANESE,

PEROXYDE OF COBALT, PEROXYDE OF NICKEL, MINIUM (*peroxyde plombeux*), and PUCE OXYDE OF LEAD (*suroxyde plombique*).

* The acid solution of the compound is next treated by sulphuretted hydrogen, and then the method is followed which has been adopted for a combination soluble in water. Attention should be paid, however, to that which I have said touching the analysis of mixed compounds insoluble in water (page 666).

* Among the combinations which are only partially dissolved by acids, there are many SILICATES, the bases of which are partially dissolved in acids, whilst the silicic acid remains insoluble (page 286).

* Among the substances which are insoluble in water and in acids are those mentioned (page 645), and likewise several simple oxydes after strong ignition, for example, OXYDE OF CHROMIUM, PEROXYDE OF TIN, TITANIC ACID, &c., and a great number of combinations of SILICIC ACID with the bases (page 284). A separate section of the following chapter will be devoted to the qualitative analysis of the combinations of silicic acid. The other substances of which I have just spoken dissolve in muriatic acid after having been fused with three times their weight of carbonate of potash or of soda.

CHAPTER XII.

COURSE OF THE QUALITATIVE ANALYSIS OF CERTAIN SUBSTANCES FREQUENTLY MET WITH IN NATURE, AND WHICH CONTAIN ONLY CERTAIN CONSTITUENTS THE ANALYSIS OF WHICH MAY BE FACILITATED BY A SPECIAL METHOD.

* AMONG the substances which consist of certain constituents only, and the analysis of which may be rendered much easier, we may place the NATIVE SILICATES and the MINERAL WATERS.

1. ANALYSIS OF THE NATIVE SILICATES.

* THE best method of analysing these compounds which constitute the greatest portion of the minerals, and distinguishing them from those which contain no silicic acid, consists in the use of the blow-pipe. In effect, by fusing them upon charcoal with microcosmic salt the silicic acid remains undissolved, and whilst the blowing is continued it floats about in the fused bead in the form of a translucid, intumesced mass (page 290).

* Most of the combinations of silicic acid contain only a small number of constituents, which generally are the same in all, and differ only in their relative proportions; wherefore they might very well be compared with the organic substances which contain likewise only a few constituents, though they so much vary in the relative proportion of the materials of which they consist. The ordinary constituents, and which consequently should always be sought for in unknown siliciferous compounds, are, independently of *silicic acid:* ALUMINA, LIME, MAGNESIA,

PROTOXYDE OF IRON, and more or less abundant traces of PROTOXYDE OF MANGANESE, an ALKALI, and WATER. Besides these, the siliceous combinations sometimes contain rare oxydes, the presence of which may often be detected before the blow-pipe; but when the latter oxydes do not exist in it, the course of the qualitative analysis of siliceous compounds is very simple. It is not even necessary when the operator has to determine the relative quantities of the constituents, to begin by the researches prescribed for the qualitative analysis, and the operator may at once proceed with the quantitative analysis; observing, of course, the rules which have been laid down in the second volume of this work, Art. "SILICIUM."

* When a siliceous combination is to be examined in the humid way, it is necessary to reduce it into very fine powder, and if muriatic acid can decompose it, it is to be treated by this acid in the manner described (page 286)[1]; but previously to this a portion must be devoted to ascertain by the method described (page 592) whether it contains WATER. Generally this portion of the combination can no longer be used in the subsequent operations of the qualitative analysis, because it may often occur that the combinations of silicic acid resist the action of muriatic acid after having been ignited, though before being ignited they may have been susceptible of being decomposed by it (page 289). The silicic acid which is separated during the decomposition is collected upon a filter and washed, and then its purity is examined. For this purpose a small portion of it is tried before the blow-pipe with soda (page 290); yet, although soda may fuse it into a limpid bead, it is not a proof of perfect purity. It is then dissolved with the help of heat in a solution

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[1] It must be remembered that perfect pulverisation is often a *sine quâ non* condition of solubility; and in all cases the greater the state of division of a substance, the more rapidly it dissolves. Hard bodies are wrapped in a piece of paper, and broken with a hammer upon an anvil, or crushed in a vice, and the particles thus obtained are then thoroughly pulverised in a mortar of porphyry or of agate; and the powder thus obtained is sometimes ground with water upon an agate table, with a mullar of the same material, and if necessary it is levigated and elutriated. Those minerals which are very hard may be first exposed to a red heat, and then suddenly quenched in cold water whilst red-hot.—ED.

of carbonate of potash or of soda. This solution is more easily effected when it has not been ignited than when it has (page 284). The liquor is decanted, in order to separate it from the undissolved portion before it gelatinises, and the operator must try to dissolve the residuum by adding a fresh quantity of solution of carbonate of potash or of soda. If the residuum now disappears the silicic acid may be considered pure: in the contrary case the liberated silicic acid was not pure: then in most cases the decomposition of the combination by muriatic acid has not been complete, and that which the alkaline carbonate has left undissolved consists generally in an undecomposed portion of the siliceous compound which has resisted the action of the muriatic acid because it was not in a sufficiently fine state of division; it should then be pulverised again, endeavouring to decompose it completely by muriatic acid. It often happens, however, that the siliceous compound which is decomposable by muriatic acid is more or less mixed with another siliceous compound on which acids have no action, and this remains undissolved when treated by a solution of alkaline carbonate. In a few rare cases, however, muriatic acid leaves traces of undissolved portions of the combination; this happens, for example, with the combinations which contain *glucina*. Glucina sometimes forms with certain metallic oxydes, for example, with peroxyde of tin, of cerium, and of manganese, combinations which are completely decomposed by acids. This point will be more amply examined further on.

* When it has been ascertained by means of the blow-pipe that the combination under examination contains much *iron*, a little nitric acid is to be poured in the muriatic acid liquor filtered from the silicic acid, with which the water which has served to wash the precipitate must not yet be mixed, and the whole is heated in order to convert the protoxyde of iron into peroxyde of iron; after which the water of the washings is added: yet no nitric acid should be added to the liquor when the combination contains no iron. A slight excess of ammonia is then added to this liquor, and the precipitate which may thus be produced is

filtered as rapidly as possible; this precipitate may consist of ALUMINA and of PEROXYDE OF IRON, if these two bases exist in the compound. If the precipitate is pure white, it is ALUMINA alone; but if it is more or less brown, it consists either of PEROXYDE OF IRON alone, or of a mixture of PEROXYDE OF IRON and ALUMINA. It is to be scraped whilst yet moist from the filter, and it is boiled with solution of pure potash, and the undissolved peroxyde of iron is filtered from the liquor. If muriate of ammonia being now poured in the filtered liquor produces a white precipitate, it is a sign that ALUMINA is present.

* If the substance contained MAGNESIA, and PROTOXYDE OF MANGANESE, portions thereof are likewise separated by ammonia, and this in so much greater proportion as the liquor in which the ammonia has been poured was less acid. If the liquor was sufficiently acid, the traces of these two substances are so trifling that they need not be taken into account in a qualitative analysis. Yet a small portion of protoxyde of manganese is sufficient to impart a brown colour after some time to the precipitate produced by ammonia, because that oxyde absorbs oxygen, and is transformed into sesquioxyde of manganese.

* If there be neither *alumina*, nor *protoxyde of iron*, the liquor filtered from the silicic acid yields no precipitate when treated by ammonia, or if an abundance of *magnesia*, or of *protoxyde of manganese* in the combination should cause one to appear, it would completely redissolve in a solution of muriate of ammonia, which does not happen when it contains *alumina* and *peroxyde of iron*.

* If to the liquor filtered from the precipitate produced by ammonia, a solution of oxalic acid and some ammonia are added, taking care that the ammonia is in slight excess, or else if a solution of oxalate of ammonia is poured into it, the LIME will then be precipitated. Its absence may be regarded as certain when oxalate of ammonia fails in producing a precipitate even after a long time. The *oxalate of lime* thrown down may often contain a little oxalate of manganese, owing to which it has

a brownish tinge when there is an excess of ammonia. The *oxalate of lime* is left at rest for some time, and then it is gently warmed in order to allow it to settle well, after which it is filtered.

* Oxalate of ammonia must now be poured in the filtered liquor in order to be sure that all the lime has been thrown down; this precaution should never be neglected. A small quantity of solution of *phosphate of soda* and a little *ammonia* are now added to a portion of this filtered liquor. (The ammonia needs not be added if already in sufficient excess). If a precipitate is thereby produced, it is a proof of the presence of MAGNESIA.

* Beginners very often fail, when the liquor contains LIME, in precipitating it completely by means of oxalate of ammonia, and are afterwards led to believe (after filtering the ammoniacal liquid from the oxalate of lime) that they now find magnesia, because of a precipitate being formed by testing with phosphate of soda; but the precipitate is often nothing else than phosphate of lime. Wherefore it is always well to examine whether the ammonio-magnesian phosphate precipitated should not perchance contain *lime*. The best way of obtaining a conclusive proof in this respect consists in dissolving the precipitate in muriatic acid, and adding a little sulphuric acid to the solution, together with a pretty large quantity of alcohol at fifty or sixty per cent., by which means a precipitate of sulphate of lime is formed, even if the proportion of lime be very small. If the precipitated magnesia contained no lime, no precipitate is thus formed. The sulphate of lime thrown down, as just said, is not generally free from magnesia. But when the phosphatic precipitate contains no lime at all, the operation just mentioned determines no precipitate.

* If the combination contains no *magnesia*, another portion of the solution, to which no phosphate of soda has been added, is evaporated to dryness, and the residuum is ignited to expel the ammoniacal salts. If during the course of the analysis no nitric acid has been used for the purpose of peroxydising the

protoxyde of iron, a platinum crucible may very well be used for igniting the dried mass. After ignition the ALKALI remains in the state of a metallic chloride. It is to be dissolved in a small quantity of water, and its nature is determined according to the rules which we have indicated (pages 659, 689). After dissolving the alkaline chloride, there ordinarily remains still a small quantity of silicic acid in an insoluble state.

* Yet when the siliceous combination contains *magnesia,* the detection of the alkali is more difficult. In that case the operator must take a portion of the solution to which no phosphate of soda has been added, and treat it as we have described (page 659). It must be remarked, however, that it is rare that the siliceous combinations, which are easily decomposed by acids, contain both an alkali and magnesia simultaneously.

* The presence of PROTOXYDE OF MANGANESE, of which only very small traces exist in siliceous combinations, is more easily recognised before the blow-pipe than in the humid way (page 65).

* If the siliceous combination is not decomposed by muriatic acid, it is reduced into very fine powder, and fused in a platinum crucible, with three times its weight of carbonate of potash or of soda. The best mode is to levigate it first. When the siliceous combination is mixed with five parts of carbonate of potash, and four parts of carbonate of soda, and the whole heated in a small platinum crucible, the flame of a good spirit-lamp is sufficient to fuse it, and completely to decompose it. It is well, however, in such a case, to take more than three times its weight of the alkaline carbonate. During the fusion a disengagement of carbonic acid is taking place, which causes projections of the mass, so that this method cannot be resorted to for a quantitative analysis.

* The mass which may be partially melted, and only partially agglomerated (page 286) is treated by water, after which an excess of muriatic acid is poured in the liquor. The aqueous liquor is green, as well as the fused mass, if it contains the least trace of protoxyde of manganese. The green liquor becomes

red by addition of a small quantity of muriatic acid, an excess of which, especially with the help of heat, in course of time discolours it under disengagement of chlorine (page 326). Wherefore the supersaturation with muriatic acid must not be effected in a platinum crucible.

* The acid liquor is evaporated to dryness in a porcelain capsula, and the residuum is treated by water, which leaves the silicic acid undissolved (page 285). As, however, magnesia, alumina, and peroxyde of iron, after having evaporated to dryness their muriatic acid solutions, and heated the residuum somewhat too strongly, might fail in dissolving completely in water, the mass which is left after the evaporation must be uniformly drenched with concentrated muriatic acid, and left in contact with it for about a quarter of an hour; water is then added, the undissolved silicic acid is separated by filtering, and the filtered liquid is treated in the same manner as the muriatic acid solution separated from the silicic acid which is obtained when siliceous substances have been decomposed by muriatic acid.

* If, however, the siliceous compound contains an alkali, its presence cannot be detected by treatment with carbonate of potash or of soda. In order to ascertain the presence or absence of the alkali in the combination, a separate operation must be performed. In qualitative analysis, a sufficient degree of accuracy is obtained by levigating the siliceous compound, and mixing it with about four or five times its weight of nitrate of baryta reduced to powder, and carefully igniting the mixture in a silver crucible, until the nitrate of baryta is decomposed. It is advisable, before mixing the nitrate of baryta in fine powder with the siliceous combination, to dry it for a long time, in order that it should not decrepitate too violently when the heat is applied. The flame of the spirit-lamp may be employed to heat the mass which undergoes a strong intumescence as soon as the nitrate of baryta begins to decompose. When this intumescence has ceased, the silver crucible is heated upon a charcoal fire as strongly as can be done without fusing the crucible.

* After ignition, the mass is softened by water, and then it is

supersaturated in a glass with muriatic acid. The acid liquor is evaporated to dryness in a porcelain capsula, and the dry mass is drenched with concentrated muriatic acid. It is then left at rest for about a quarter of an hour, water is poured upon it, and the silicic acid being insoluble, is separated by filtering. A little sulphuric acid is now added to the filtered liquid so as to precipitate the greatest portion of the baryta, but not all, in the state of sulphate of baryta, and it is then supersaturated, without filtering it, with solution of carbonate of ammonia, which precipitates the baryta which is still held in solution, as well as the alumina and peroxyde of iron of the siliceous combination. The precipitate is then separated by filtering, and the filtered liquid is concentrated by evaporation, by which means the greatest portion of the excess of carbonate of ammonia is volatilised. A little sulphuric acid is now added to precipitate the baryta which might still remain, because carbonate of baryta is not absolutely insoluble in water; yet, ordinarily, the solution contains baryta, only when the precipitate produced by carbonate of ammonia has been washed for a long time. It is particularly necessary to avoid using too much sulphuric acid.

* After separating the precipitate (if any is produced) by filtering, the liquor is evaporated to dryness, and the dry residuum is ignited in order to decompose the ammoniacal salts. The alkali contained in the combination remains then in the state of sulphate, and its nature may be subsequently determined. If the combination contains several alkalies, their presence may be ascertained by the means which have been indicated in Chapter VIII.

* If magnesia exists in the compound, it is found in the state of sulphate, with the sulphate of alkali, from which it may be separated in the manner described in Chapter VIII.

* The decomposition of siliceous compounds must not be effected by nitrate of baryta in quantitative analysis, as will be shown in the second volume, but in qualitative analysis it is more advantageous to employ it than carbonate of baryta.

* Another method of decomposing, in qualitative analysis,

siliceous compounds which contain an alkali, and which cannot be decomposed by acids, is the following:—The combination is reduced into very fine powder by levigation, and the powder is mixed in a platinum capsula or crucible, with about five parts of fluor-spar finely pulverised, and free from all metallic substance. To this mixture concentrated sulphuric acid is added to creamy consistence, and the whole is well stirred with a platinum wire, and not of course with a glass tube. The platinum vessel is now heated to incipient redness, so that the excess of sulphuric acid volatilises along with fluoride of silicium gas, and hydrofluoric acid gas.

* After cooling, the ignited mass is placed in an ordinary glass, water is poured upon it, and it is digested therein with the help of heat for a long time. That which remains insoluble consists for the most part of sulphate of lime. The residuum is separated by filtering and washed several times. A solution of carbonate of ammonia, or of oxalate of ammonia and of pure ammonia, is now added to the filtered liquid, in order, completely, to precipitate the peroxyde of iron, alumina, and the portion of lime which the sulphuric acid has not separated. Some time is allowed to elapse in order to permit the precipitate to settle well at the bottom, and the mass is then filtered. The filtered liquor is now evaporated to dryness, and the residuum ignited in a platinum crucible. This ignited residuum consists of sulphate of alkali, which may, however, be mixed with sulphate of magnesia if that body be present. With a few peculiar directions, which will be given in the second volume, this method is applicable to quantitative analysis, yet it is advisable to resort to it only for the purpose of detecting the presence of an alkali in siliceous compounds.

* The best method for qualitative and quantitative analysis for the detection and determination of the alkali contained in siliceous compounds which are not attacked by muriatic acid, consists in decomposing it by concentrated hydrofluosilicic acid. This method can, however, be resorted to only with the help of a platinum retort, because hydrofluoric acid does not keep well,

and cannot be rapidly prepared in the pure state with pulverised fluor-spar and concentrated sulphuric acid except by distillation in a platinum retort, but as a platinum retort cannot always be procured, one of lead may be substituted.

* Hydrofluoric acid, in order to effect this decomposition, must be concentrated. The silicic combination under examination is first reduced into fine powder by levigating. The powder is dried, put in a platinum crucible, and the acid is poured upon it, which produces a violent reaction, and the whole is stirred with a stout platinum wire; sulphuric acid is then cautiously added, and evaporated to dryness, taking care, towards the end, to heat the crucible to incipient redness, in order to volatilise completely the fluoride of silicium gas which will have formed, and also the excess of hydrofluoric and of sulphuric acids. A small quantity of concentrated muriatic acid may be poured upon the residuum in order to render the alumina, peroxyde of iron, and magnesia, soluble in water, because the combinations of these substances become insoluble after having been strongly heated.

* This method of decomposing siliceous combinations by hydrofluoric acid enables the operator easily to detect the presence of all the constituents of the compound except silicic acid, which volatilises in the state of fluoride of silicium gas. A quarter of an hour after having drenched the mass with muriatic acid, water is poured upon it, which generally leaves a little silicic acid undissolved. Yet it must not be filtered directly, because a small quantity of silicic acid may easily pass through the filter and render the liquor turbid.

* If the combination contains LIME, the residuum left by water must be well washed for the purpose of dissolving the sulphate of lime produced. Ammonia is then added to the solution, which precipitates the ALUMINA and PEROXYDE OF IRON. The liquor is filtered, and the addition of oxalic acid and ammonia precipitates the LIME. The liquor is then filtered from the precipitate and evaporated to dryness. The residuum is ignited in order to volatilise the ammoniacal salts, after which the alkali remains in the state of sulphate, which,

however, may be mixed with *sulphate of magnesia,* if the combination contained any MAGNESIA.

* There is a small number of siliceous combinations which can be completely decomposed neither by acids nor by fusing with an alkaline carbonate, and which resist also the action of hydrofluoric acid; we have given their names (page 289). To analyse them qualitatively, the following method is resorted to:—The combination is reduced into very fine powder by levigation, the powder is put in a silver crucible, and a very concentrated solution of pure potash being poured upon it, the whole is evaporated to dryness, taking care to stir it constantly with a silver spatula. The residuum is next ignited in the crucible with as high a heat as the crucible can bear without fusing. The ignited mass is then softened with water, and washed in an ordinary glass, and treated in the same manner as the siliceous combinations which have been ignited with an alkaline carbonate.

* Several combinations, however, are found in nature, which besides the constituents which we have just enumerated, and which are of most frequent occurrence, contain also other constituents of a rare nature. These constituents, more rarely met with in siliceous compounds, exist in them only in very small quantities, so that it often happens that their presence is overlooked in qualitative analysis. We will not only name the siliceous combinations, in which they have hitherto been found, but give also the means by which their presence can be best ascertained.

1. BARYTA.—It has hitherto been found only in the BARYTIC HARMOTOME, and in BREWSTERITE. The best method of isolating it from the muriatic acid liquor filtered from the silicic acid consists in pouring sulphuric acid in the liquor, by which it is precipitated in the state of sulphate of baryta, which is insoluble. If the mineral contained at the same time much LIME, a great quantity of sulphate of lime is simultaneously precipitated, which, however, might be separated by water alone from the sulphate of baryta. Should, however, the combination

contain strontia or protoxyde of lead, these bases would likewise be precipitated from the muriatic acid solution by sulphuric acid. We have said (page 678) how baryta, in the state of sulphate, can be distinguished from these two oxydes.

* 2. STRONTIA.—Connel detected it conjointly with baryta and lime in Brewsterite. It is precipitated by sulphuric acid from the liquor filtered from the silicic acid; and the methods described (page 658) are then adopted in order to separate it from the baryta and lime.

* 3. GLUCINA is found in the EMERALD, EUCLASE, CYMOPHANE, and HELVINE. In the three first of these compounds it is accompanied by alumina, with which it may be easily confounded. When, in the course of an analysis, ammonia is poured in the liquor filtered from the silicic acid, the precipitate produced by this re-agent contains the glucina of the combination. In order to demonstrate the presence of this earth, the precipitate, whilst still moist, is dissolved in the smallest possible quantity of muriatic acid, and to this concentrated solution a tolerably large excess of solution of carbonate of ammonia is added, with which the precipitate is left in contact for some time, and preferably, in a stoppered flask. After filtering the liquor from the insoluble residuum, the glucina is contained in the filtered liquor from which it may be obtained by evaporating it, and tested by the re-agents, as we have said (page 48).

* HELVINE contains so much protoxyde of manganese, that unless the glucina precipitated by ammonia be filtered rapidly, a certain quantity of manganese falls down with it, from which, however, it may be separated by a solution of pure potash.

* *Glucina* exists also in small quantity in some varieties of gadolinite, in the analysis of which mineral it may be separated from *yttria* by solution in pure potash.

* But, whereas glucina has much resemblance with alumina, it is necessary to examine whether the alumina which has been obtained in analysing siliceous compounds, contains any of it. It should, therefore, be tested before the blow-pipe with solution

of nitrate of cobalt (page 47). If a pure blue colour is thus produced, the alumina is free from glucina; if, on the contrary, it is a dirty blue, it is advisable to submit the alumina to the action of the appropriate re-agents for the detection of glucina.

* 4. THORINA.—This earth has been found by Berzelius in thorite alone. The following method was resorted to by him for the purpose of demonstrating its presence and separating it from the other constituents:—The mineral was first reduced into powder, and decomposed by muriatic acid. The liquor filtered from the silicic acid was precipitated by ammonia, the precipitate dissolved in muriatic acid, and the acid liquor was freed by a current of sulphuretted hydrogen from traces of protoxyde of lead and of peroxyde of tin. The liquor filtered from these precipitated sulphurets was evaporated to dryness, the residuum redissolved in water, and the solution boiled with a solution of potash, which dissolved a trace of alumina, and precipitated the thorina. To separate it from the peroxyde of iron, protoxyde of manganese, and peroxyde of uranium, it was redissolved in muriatic acid, and the solution was next neutralised by ammonia, and concentrated by evaporation. It was then left in contact with crystals of sulphate of potash as long as it continued to dissolve that substance; the pulverulent precipitate which was thus obtained, was washed with a saturated solution of sulphate of potash, in which the double salt of thorina is insoluble (page 51), then dissolved in hot water and again precipitated by a solution of potash.

* 5. YTTRIA.—It is met with in GADOLINITES, and also in ORTHITE, and PYRORTHITE. When ammonia is added to the solution filtered from the silicic acid, yttria exists in the precipitate which is thus formed. If this precipitate be treated by a solution of pure potash, the yttria will be thus separated from the alumina and glucina which it might contain. That which has been left undissolved by the potash is dissolved in muriatic acid; the solution is diluted with a small quantity of water, and if a crystalline crust of sulphate of potash be now plunged in it, the protoxyde of cerium, which gadolinites and orthites always

contain, will be precipitated. The crystals of the salt must be left in contact with the liquor for twenty-four hours, the precipitate which is thus formed is washed with a saturated solution of sulphate of potash in which protoxyde of cerium is insoluble, and **YTTRIA** soluble (page 53). The filtered liquor then contains the yttria, which may be precipitated by ammonia. This re-agent, however, precipitates, at the same time, peroxyde of iron which exists in the minerals in question in the state of protoxyde of iron. These two substances may be sufficiently well separated from each other by saturating exactly the acid liquor with ammonia, and then adding a solution of succinate of ammonia which precipitates the peroxyde of iron in the state of succinate of iron [persuccinate of iron]. An excess of ammonia being then poured in the filtered liquor precipitates the yttria therefrom.

6. **PROTOXYDE OF CERIUM** is met with in **CERITE** and **CERINE**, also in **GADOLINITES**, **ORTHITE**, and **PYRORTHITE**, and in general in all the minerals which contain yttria, which it almost always accompanies. We have just said in speaking of yttria, which it much resembles, how they can be separated from each other.

* 7. **ZIRCONIA.**—It is an essential constituent of **ZIRCON**, and according to Stromeyer, of **EUDIALITE**.

* After having decomposed the zircon by treatment with pure potash, or pure soda, which operation is difficultly performed, the ignited mass is treated as usual by muriatic acid, and the silicic acid is separated by evaporation; but a very gentle heat only must be used, because without this precaution there might remain a large quantity of zirconia in an undissolved state along with the silicic acid. The silicic acid is separated by filtering; ammonia is poured in the filtered liquid in order to precipitate the zirconia. If the zircon under examination contains traces of peroxyde of iron, they are precipitated along with the zirconia.

* In eudialite, zirconia is combined not only with silicic acid, but likewise with lime, soda, peroxyde of iron, sesquioxyde of manganese, and a small quantity of chloride of sodium. After decomposing it by muriatic acid, and separating the silicic acid, zirconia is precipitated by ammonia, as in the analysis of

the zircon, and the peroxyde of iron is precipitated simultaneously with the zirconia. In qualitative analysis, peroxyde of iron may be separated tolerably well from zirconia by collecting the precipitate on a filter, and igniting it strongly. The zirconia is thereby rendered insoluble in muriatic acid (page 58), by which acid the greatest part of the peroxyde of iron may thus be separated from the ignited mass. The following method which is also employed in quantitative analysis is better: it consists in pouring tartaric acid in the muriatic acid solution of zirconia and of peroxyde of iron, for in presence of that acid these two bases are not precipitated from the solutions by the alkalies (pages 58, 92); by pouring afterwards hydrosulphuret of ammonia in the solution previously supersaturated with ammonia, the peroxyde of iron is precipitated in the state of sulphuret of iron. In order to obtain the zirconia contained in the liquor filtered from the sulphuret of iron, the liquor must be evaporated to dryness, and the dry residuum ignited in contact with the air until the carbon of the tartaric acid is burnt. The zirconia is then left in the state of a powder insoluble in acids.

* 8. OXYDE OF ZINC.—This oxyde is found in the SILICATE OF ZINC. In order to detect it in this combination, the silicic acid is first separated from the muriatic acid solution by filtering; it is freed from the traces of protoxyde of lead and peroxyde of tin which it contains by means of sulphuretted hydrogen, and the liquor is next supersaturated with ammonia; after which hydrosulphuret of ammonia is added, which produces a white precipitate of sulphuret of zinc, which may easily be recognised as such. Oxyde of zinc is less easily detected by the blow-pipe in silicate of zinc, because the fumes of zinc are produced only with difficulty when treated with soda upon charcoal in the interior flame.

* 9. OXYDE OF NICKEL forms one of the constituents of PIMELITE, and it exists also but in very small quantity in crysoprase, and according to Stromeyer, in some species of OLIVINE. It may be detected by the blow-pipe in PIMELITE when treated by borax and by microcosmic salt (page 82);

a great quantity of nickel reduced into the metallic state is obtained by treating it with soda upon charcoal. In the qualitative analysis of other minerals, the best method of detecting small quantities of oxyde of nickel consists in pouring an excess of ammonia in the muriatic acid liquor filtered from the silicic acid, and then to add a little hydrosulphuret of ammonia to the filtered liquor. A very small black precipitate of sulphuret of nickel is thereby produced, which may be subsequently tested to identify it.

* 10. Oxyde of cadmium.—In order to detect this oxyde, which is sometimes contained in some varieties of silicated zinc, the best method is to dilute with water the muriatic acid liquor separated from the silicic acid by filtering, and to pass a current of sulphuretted hydrogen through it, a yellow precipitate of sulphuret of cadmium will thereby be produced, accompanied however by traces of lead and of tin, if the combination contained any acid, and which are precipitated at the same time in the state of sulphuret.

* 11. Protoxyde of lead.—Traces of protoxyde of lead have been found in several siliceous combinations, as, for example, in THORITE and SILICATED ZINC, &c. These traces of oxyde of lead may be contained entirely in the muriatic acid liquor filtered from the silicic acid. More considerable quantities of oxyde of lead would dissolve only partially in the state of chloride of lead, and could not be completely separated from the silicic acid by washing. For this reason nitric acid is employed instead of muriatic acid, in order to decompose the combination, and then before treating the liquor by ammonia, a current of sulphuretted hydrogen is passed through it, which precipitates the oxyde of lead in the state of sulphuret of lead, which may be subsequently recognised as such. Ordinarily it is necessary further to treat the liquor by hydrosulphuret of ammonia, in order to separate traces of sulphuret of tin, because the traces of oxyde of lead in siliceous compounds are generally accompanied by traces of peroxyde of tin.

* 12. Oxydes of uranium.—Oxyde of uranium is the base

of the mineral called PITCHBLENDE[1]. It is also found in small quantity in several siliceous combinations, such as THORITE. In order to detect traces of oxyde of uranium in these substances, the silicic acid must be separated, and the filtered liquid being supersaturated with ammonia, the precipitate resulting therefrom is dissolved in muriatic acid, and potash is poured in the solution. The precipitate produced by this re-agent is next put to digest in a concentrated solution of carbonate of ammonia, which dissolves the oxyde of uranium. The solution may be evaporated to dryness, and the dry mass is put to digest in dilute acetic acid, which dissolves the oxyde of uranium. The solution has a yellow colour, and ammonia produces therein a yellow precipitate, which behaves before the blow-pipe as we have said (page 112).

* 13. PROTOXYDE OF COPPER.—This oxyde is one of the principal elements of DIOPTASE, and SILICEOUS MALACHITE. After having decomposed these substances by muriatic acid, the acid liquor filtered from the silicic acid contains no other essential constituent principle than protoxyde of copper. This oxyde has been found also in very small quantity in some species of IDOCRASE in Norway, in CERINE, and ALLOPHANE, and in ALUMINOUS SCHISTUS, in which the blow-pipe is already sufficient to render its presence visible (page 122). In the humid way, however, in order not to overlook any trace of oxyde of copper, it is necessary to treat the mineral with some alkaline carbonate, to decompose the ignited mass with muriatic acid, separate the silicic acid by filtering, and pass a current of sulphuretted hydrogen through the filtered liquor which will precipitate the traces of oxyde of copper in the state of sulphuret of copper.

* 14. PEROXYDE OF TIN.—This oxyde is found in a great number of siliceous combinations, yet it never forms an essential constituent of these substances, so that traces only should be

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[1] Messrs. Wöhler and Swanberg have found *vanadium* in pitchblende, which hitherto had escaped detection. To obtain it, pitchblende should be heated to redness with carbonate of potash and a little nitrate of potash; treating the mass with water will yield a solution, from which ammonia precipitates vanadic acid in the state of vanadate of ammonia.—Ed.

looked for. Berzelius found traces of peroxyde of tin in some species of **EMERALD**, in **EUCLASE**, **SILICATED ZINC**, and in **THORITE**. But doubtless this oxyde exists in a very great number of other minerals, but hitherto its presence has not yet been detected.

* The best manner to ascertain its presence consists in passing a current of sulphuretted hydrogen in the muriatic acid liquor, filtered from the silicic acid; the peroxyde of tin is thereby converted into sulphuret of tin, and is precipitated, even though the solution contains only a very small proportion of it. In such a case, however, the precipitation does not take place immediately, but only after a certain time; and especially by warming the acid liquor (page 179).

When the siliceous combination contains at the same time protoxyde of lead or another metallic oxyde susceptible of being precipitated from the acid solution in the state of metallic sulphuret by sulphuretted hydrogen, which may generally be recognised by the colour of the precipitate, the metallic sulphuret obtained should be treated by hydrosulphuret of ammonia, which dissolves sulphuret of tin. This solution of sulphuret of tin is evaporated to dryness in a platinum crucible, and the residuum is ignited; peroxyde of tin is thus obtained, which must be treated before the blow-pipe upon charcoal with soda in order to obtain the tin in the metallic state.

* There are, however, a few cases in which the traces of peroxyde of tin form with certain bases, especially with glucina, combinations which after the decomposition of the siliceous compound dissolve only incompletely, or, at least, with great difficulty, in muriatic acid. Such is the case when euclase and emerald, which contain peroxyde of tin, are fused in the ordinary way with carbonate of alkali. After having saturated the ignited mass with muriatic acid there remains a white powder, which may be easily distinguished both from a residuum of the mineral and from the liberated silicic acid, and which may likewise be easily separated from the latter body. This white powder is a combination of peroxyde of tin with glucina, which is easily dissolved by water after fusion with bisulphate of

potash. A current of sulphuretted hydrogen passed through this solution precipitates the peroxyde of tin in the state of sulphuret of tin, which yields a globule of tin when treated before the blow-pipe with soda upon charcoal.

* When the siliceous combination which contains traces of peroxyde of tin is treated immediately before the blow-pipe with soda upon charcoal, no sensible traces of reduced tin can be obtained.

* 15. OXYDE OF CHROMIUM.—This oxyde is frequently met with in siliceous compounds, but in most cases it forms only a non-essential constituent. Several of these combinations, for example, the **PERUVIAN EMERALD**, owe their fine green colour to its presence; this green colour, however, is not always due thereto, as for example, in the emerald of Siberia, and of Salzbourg. But oxyde of chromium does not always impart a green colour to siliceous compounds, for the blood-red colour of several of these combinations is referrible to the presence of this oxyde; such is the case for example with the mineral called **PYROPE**. These siliceous combinations to which chromic oxyde imparts a blood-red colour, have the property of becoming black and opaque merely by the action of heat; as they gradually cool, they assume by transmitted light, a yellowish tinge, or a pure chrome-green colour, and after complete cooling they re-assume their original colour. Small quantities of oxyde of chromium have also been found in **CHATOYANT SPAR** and some species of **SERPENTINE**.

* Even when the quantity of oxyde of chromium in siliceous compounds is very small, its presence may often be detected by means of the blow-pipe alone, because those combinations communicate to the flux of borax or of microcosmic salt, after complete cooling, a chrome-green colour, which, however, is generally very feeble as, for example, by operating upon the Peruvian emerald. Yet when the combination contains at the same time a large quantity of peroxyde of iron, the fluxes derive from it the ordinary green colour produced by iron, and consequently prevent the manifestation, or at least the detection, of the chrome-green colour.

* When the combination can be decomposed by muriatic acid the presence of oxyde of chromium may be ascertained in the humid way in the precipitate which ammonia produces in the muriatic acid liquor filtered from the silicic acid. Even when chromium exists in the siliceous compound in the state of chromic acid, it is contained in the state of oxyde of chromium in this precipitate, which may also contain peroxyde of iron, alumina, &c. It is dried, and then boiled, if it contain alumina, with a solution of potash, which dissolves the alumina, and leaves the peroxyde of iron and of chromium. These two oxydes may then be fused in a small porcelain crucible with nitrate of potash, and the fused mass is treated by water, which dissolves the chromate of potash produced, and leaves the peroxyde of iron. The solution is then neutralised by nitric acid, and the chromic acid is precipitated by means of nitrate of mercury, of nitrate of baryta, or of nitrate of lead. The precipitate obtained is treated before the blow-pipe, to put the existence of chromium beyond doubt.

* When a siliceous combination containing oxyde of chromium is decomposed by fusing it with carbonate of alkali, it frequently happens that, after treating the fused mass by muriatic acid, the silicic acid obtained has a brown tinge, and is mixed with some brown chromate of oxyde of chromium. If, however, this brown silicic acid be fused with nitrate of potash in a small porcelain crucible, and the fused mass be digested in water and muriatic acid, the liquor evaporated to dryness, and the dry residuum treated as usual with muriatic acid and water, the silicic acid which remains is white, whilst the solution contains the oxyde of chromium. The chromic acid may be still more easily and completely reduced into oxyde of chromium by adding a little alcohol whilst the muriatic acid liquor is evaporating to dryness.

* 16. Titanic acid.—Titanic acid in combination with silicic acid enters as an essential constituent only in the mineral called *sphène,* which besides this substance contains *lime* also. Titanic acid exists in very large quantities in this mineral, and yet its

presence cannot be very easily detected with the blow-pipe by the colour which that acid ordinarily communicates to the fluxes, though the presence of silicic acid and of lime do not prevent the manifestation of that characteristic colour. A bead of borax when treated with some *titanite* in the interior flame of the blow-pipe does not turn blue, and a bead of microcosmic salt is coloured blue by that substance only when the mixture is left exposed for a long time to the action of the reducing flame.

* Very feeble traces of titanic acid are also found as a constituent, but not an essential one, of several minerals, as is the case with peroxyde of tin. It has been met with in CYMOPHANE, in CYANITE, in some species of MICA and in ACHMITE. When these minerals are fused in the ordinary way, with carbonate of alkali, and the fused mass subsequently treated by muriatic acid and water, the titanic acid dissolves in the muriatic acid in the state of titanate of alkali. If now the acid liquid be evaporated at a very gentle heatin order to promote the separation of the silicic acid, the alumina, peroxyde of iron, and titanic acid, which had re-dissolved, are precipitated when ammonia is added to the liquor filtered from the silicic acid. When this precipitate being first dried, is ignited, and then treated by muriatic acid, the greatest portion of the titanic acid remains undissolved, and may be recognised as such before the blow-pipe, although it is not perfectly pure, but has a slight reddish colour from the admixture of a certain quantity of peroxyde of iron. If after having fused the mineral with the alkaline carbonate, too strong a heat has been employed in order to promote the separation of the silicic acid from the muriatic acid liquor, it is to be feared, especially if the evaporation has been driven to boiling, that when the traces of titanic acid will come to be treated by muriatic acid and water, the greatest part of this acid will not dissolve, and will remain with the silicic acid.

* 17. TANTALIC ACID.—Hitherto it has been found by Berzelius only as a non-essential constituent of some species of EMERALD. When this mineral is heated with carbonate of alkali,

and subsequently decomposed by muriatic acid, the traces of tantalic acid do not remain mixed with the silicic acid, as might be supposed, but are dissolved conjointly with the glucina and alumina, in the muriatic acid liquor filtered from the silicic acid. If the glucina be dissolved in a solution of carbonate of ammonia, the traces of tantalic acid follow this earth, but they may be separated from each other by dissolving the glucina in muriatic acid after calcining. By this treatment the tantalic acid remains mixed with some silicic acid.

* 18. BORACIC ACID.—It has been met with in a great number of minerals, more or less abundantly. It forms one of the principal constituents of the minerals called DATHOLITE and BOTRYOLITE. It has been found in smaller quantity in the several species of TOURMALINE and of AXINITE. Turner, using the blow-pipe, as we have said, (page 282), detected likewise the presence of this acid in the Brazilian TOPAZ, and also in a GARNET of Norway (colophonite), and C. G. Gmelin discovered it in the same manner in some species of MICA, of LEPIDOLITE, and of PINITE. According to Kersten, however, the blow-pipe is not a perfectly certain method of detecting boracic acid, because there are several other minerals which contain no trace of this acid, as for example, several species of fluor-spar, and which give an analogous reaction when treated in this manner.

* The most trustworthy method of ascertaining the presence of boracic acid in the siliceous combinations which are susceptible of being decomposed by an acid, consists in reducing them to powder, and decomposing them by concentrated sulphuric acid, after which, and without separating the silicic acid, alcohol is added to the liquor, and is set fire to. The green colour of the flame testifies the presence of boracic acid. Muriatic acid must not be used instead of sulphuric acid for the purpose of decomposing the siliceous combinations, for the reasons which have been given (page 281).

* If the siliceous combination resists the action of acids, it must be reduced into very fine powder, and fused with about three times its weight of carbonate of potash or of soda; the

fused mass is then decomposed by sulphuric acid diluted only with a small quantity of water, and alcohol is then poured upon it, which being inflamed, will burn with a green flame if the smallest quantity of boracic acid be present.

* 19. PHOSPHORIC ACID.—This acid is met with in small quantities in siliceous combinations. Hitherto it has been found only in the minerals called SORDAWALITE, and in some species of LEPIDOLITE. It is proboble, however, that it exists also in several other siliceous combinations, for its presence can often be easily overlooked unless especially sought for. This acid appears to exist in several siliceous combinations which contain small quantities of the compounds of fluorine.

* In order to detect phosphoric acid in these combinations, whether they are susceptible or not of being decomposed by acids, they are fused with three or four times their weight of carbonate of soda or of potash, and the fused mass is treated by water, which dissolves only the excess of the alkaline carbonate, and also the phosphate of alkali produced, when the bases contained in the combination under examination are insoluble in the alkaline carbonate.

* The presence of phosphoric acid in the solution, even though the quantity be very small, is recognised in the following manner: —The solution must first be supersaturated with nitric acid, or better still, with acetic acid, and a solution of acetate of lead is next added, which produces a precipitate of phosphate of lead, which may be easily recognised as such before the blow-pipe (page 262). Nitrate of silver may also be used for the purpose of detecting phosphoric acid in the solution saturated with nitric acid.

It is impossible with the blow-pipe to detect the presence of phosphoric acid in siliceous compounds in the manner described (page 270), because its quantity is always too small to permit the performance of that experiment.

* 20. CARBON.—Of all the siliceous combinations which exist in nature, that called PYRORTHITE is the only one which contains carbon in considerable quantity, and its presence may be

ascertained by heating that mineral gently before the blow-pipe, and making it red-hot on one point: it then catches fire, and continues to burn by itself without either flame or smoke, after which the mineral is grey, or greyish-white. Pyrorthite being mixed with nitrate of potash, deflagrates also when heated, as is the case with all the substances which contain carbon.

* Small quantities of carbon, or rather of carbonised organic substances, the composition of which is not yet known, are found in a vast number of siliceous combinations, and are the cause of those combinations turning black when heated in a little mattrass upon a spirit-lamp. The black colour disappears by applying heat in the open air, because the carbon can then burn. This is especially the case with the siliceous combinations which contain simultaneously much magnesia and water, for example, in PIERRE DE LARD, MEERSCHAUM, PICROSMINE, PYRALLOLITE, SERPENTINE, AGALMATOLITE, PIMELITE, CHONDRODITE, COUPHOLITE.

* Some siliceous combinations contain CARBONIC ACID, but it is generally owing simply to a mixture of carbonate of lime or of other carbonates. These minerals effervesce when, after having been pulverised, muriatic acid is poured on the powder.

* 21. FLUORINE.—This substance is contained in pretty large proportion in the TOPAZ, CHONDRODITE, and in some species of MICA, especially those which contain lithia. Smaller quantities of fluorine have been found in a very great number of other siliceous combinations, especially in most species of MICA, though not in all; in almost all the species of AMPHIBOLE, in CARPHOLITE, APOPHYLLITE, and some species of CHABASIE and of SCAPOLITE. The blow-pipe employed as we have said (page 441), is generally sufficient to detect the presence of fluorine in some of those combinations, but only in those which contain at the same time a more or less considerable quantity of water. If, however, they do not contain a trace of water there is danger of overlooking even pretty large proportions of fluorine. The method indicated (page 440), must then be resorted to.

* When the operator thinks that he has detected, by means of the blow-pipe, that a combination of fluorine is contained in

the siliceous compound under examination, its existence must be placed beyond doubt by a more rigorous research, especially if there be only traces of fluorine, and if the siliceous combination be not decomposable by sulphuric acid. This may be ascertained by the method which has been described, (page 440). If this method be followed, a precipitate of fluoride of calcium is obtained, even when the combination contains traces only of fluorine. The fluoride of calcium thus obtained must now be decomposed by sulphuric acid in the usual way, as we have said (page 437), in order to see whether the glass has been corroded.

* We should remark, however, that the precipitate produced by chloride of calcium may contain, besides fluoride of calcium, other insoluble combinations of lime with acids if such do exist in the siliceous compound. The fluoride of calcium may be accompanied in this precipitate by phosphate of lime especially, and generally by combinations of lime with the acids which have been enumerated, (page 664). The operator must look most carefully for phosphoric acid, because, as we have already said, (page 721), this acid exists very frequently in minerals which contain combinations of fluorine. Therefore, after having decomposed the precipitate by sulphuric acid in a platinum crucible in order to ascertain the presence of fluorine by its corrosive action upon glass, the residuum is treated by a large quantity of water which dissolves the excess of sulphuric acid and the sulphate of lime produced, and leaves the phosphate of lime, which may be submitted to an ulterior examination.

* 22. CHLORINE.—Chlorine has been found, but always in a very small quantity, in several siliceous combinations, especially in SODALITE, EUDIALITE, and PYROSMALITE. The presence of a combination of chlorine in the siliceous combinations which are decomposable by acids, may be detected by decomposing them by nitric acid, carefully avoiding the application of heat as much as possible; it is best therefore to leave the nitric acid to act upon the pulverised mineral in a flask with a glass stopper. After having separated the liquor from the silicic acid by filtering, solution of nitrate of silver is added, which precipitates the

chlorine in the state of chloride of silver, which may be easily recognised as such. If the operator wishes to detect the other constituents, the liquor is filtered in order to separate the chloride of silver, and muriatic acid is added in order to eliminate the excess of oxyde of silver employed, after which the analysis proceeds in the usual way. The three minerals above-named are decomposable by nitric acid, yet pyrosmalite is decomposed by that acid only with difficulty, and a gentle heat must be applied.

* If the siliceous compound resists the action of acids, it must be fused with carbonate of alkali, which, of course, must be quite free from chloride. The fused mass is then treated by water, which will dissolve both the excess of the alkaline carbonate and the chloride of potassium or of sodium produced; the alkaline solution must be supersaturated with nitric acid, and solution of nitrate of silver being now added, will form a precipitate of chloride of silver.

* The presence of *chlorine* in siliceous compounds may very well be ascertained by means of the blow-pipe, as we have indicated (page 424), but the analysis in the humid way should never be neglected, for it is the only method which can give an accurate result.

* 23. SULPHUR.—This substance exists in some siliceous compounds in the state either of metallic sulphuret or of sulphate. It is found in the first of these states in HELVINE, which contains it in the state of sulphuret of manganese, in which it may be easily recognised by the disengagement of sulphuretted hydrogen, produced when its decomposition is effected by muriatic acid. A portion at least of sulphur appears also to exist in the state of metallic sulphuret in HAÜYNE, NOZIAN, and LAZULITE; for these minerals, whilst being decomposed by muriatic acid, exhale an odour of sulphuretted hydrogen gas, which, however, is very feeble in the case of nozian.

* If sulphur exists in the state of sulphuret in a siliceous combination which cannot be decomposed by muriatic acid with disengagement of sulphuretted hydrogen, its presence can be detected only by treatment with fuming nitric acid, which will

then produce sulphuric acid. In such cases the siliceous combination may also be fused with carbonate and nitrate of alkali, treating the fused mass with water, and after super-saturating the liquor with muriatic acid, the presence of sulphuric acid may then be detected by testing with chloride of barium.

* Sulphur exists in the state of SULPHURIC ACID in some siliceous combinations. Those called HAÜYNE, NOZIAN, and LAZULITE contain not only a metallic sulphuret, but sulphuric acid also; for if after having decomposed these minerals by muriatic acid, chloride of barium is poured in the solution filtered from the silicic acid, a precipitate of sulphate of baryta is produced. It is necessary, however, to wash the silicic acid well, because these minerals contain lime which, after decomposition by muriatic acid, forms sulphate of lime, which is very sparingly soluble in water.

* When sulphuric acid exists in siliceous combinations which cannot be decomposed by acids, the compound must be reduced to very fine powder, fused with carbonate of potash or of soda, and the fused mass is then treated by water; the solution contains the excess of carbonate of alkali and the *sulphate* of alkali formed. The presence of sulphuric acid may therefore be easily detected by solution of chloride of barium subsequently to the super-saturating with muriatic acid.

* In the siliceous combinations which contain sulphur or sulphuric acid, but which do not at the same time contain any or very small quantities only of metallic oxydes properly so called, the presence of sulphur may be detected by means of the blow-pipe, by mixing the mineral with soda and exposing it upon charcoal to the action of the interior flame. A turbid bead may thus be frequently obtained, which becomes red on cooling. This process, however, does not succeed with HELVINE, on account of the great quantity of manganese which it contains. But the presence of sulphur may always be recognised by the blow-pipe in those combinations, by treating them upon charcoal with an excess of soda, projecting the red-hot mass upon a piece of silver,

and moistening it a little, in which case the silver assumes a brown or a black colour.

2. QUALITATIVE ANALYSIS OF MINERAL WATERS.

The salts which have hitherto been found in mineral, saline, and pump or well waters, contain the following bases and acids :—

Bases.—*Potash, soda, lithia, ammonia, strontia, lime, magnesia, alumina, protoxyde of manganese, protoxyde of iron, oxyde of zinc,* and *protoxyde of copper.*

Acids.—*Sulphuric acid, sulphurous acid, nitric acid, carbonic acid, boracic acid, phosphoric acid, silicic acid,* and besides these, *chlorine, fluorine, bromine, iodine,* and *sulphur,* united to the metal of the above bases.

* But all these constituents are not met with simultaneously in one kind of mineral waters, and some of them exist therein in so small a quantity that it is very easy to overlook them in the course of a qualitative analysis. It is therefore advisable in all cases first to test for the more abundant, and afterwards to look for the traces of the rarer constituents.

* When the operator has in view to make a quantitative as well as qualitative analysis, the presence of several substances which exist only in very trifling proportions may be detected whilst analysing quantitatively, so that the qualitative analysis may to a great extent be dispensed with at least as a separate operation.

* The research of the principal constituents of a mineral water is not difficult, and it may be performed in a short time.

* A fresh quantity of water is generally taken for the examination of each constituent, and the operation is conducted as follows :—

1. DETECTION OF ACIDS.

* A. A few drops of tincture of litmus newly prepared[1] is added to the water under trial. If the liquor turns red it is generally

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[1] Tincture of litmus may be kept good for an exceedingly long time, by mixing it with some wood naphtha, or with alcohol.—Ed.

a proof of the presence of free CARBONIC ACID, which, however, is placed beyond doubt by mixing equal quantities of tincture of litmus and of mineral water, which has previously been boiled for a long time. If the red colour produced in the first experiment is not produced in the second, it is a proof that the water contained free carbonic acid[1]. It often happens that the boiled mineral water renders reddened litmus paper slightly blue.

* Free carbonic acid is likewise detected in mineral water by adding a small quantity of lime-water thereto. If a precipitate be then produced, which the addition of a large quantity of mineral water causes to disappear, it is a proof that it contains either free carbonic acid or bicarbonate of alkali[2]. Most mineral waters contain carbonic acid combined with alkalies and earths, in the state of bicarbonate, but frequently also in the state of free carbonic acid. The latter is detected, as we have just said, by means of tincture of litmus. If it contains bicarbonates only, and no free carbonic acid, it does not redden litmus paper.

* If the mineral water contain no bicarbonates of alkalies, but bicarbonates of earths only (such as of lime, and of magnesia), and no free carbonic acid, the precipitate produced by lime water does not disappear by the addition of a large quantity of mineral water.

* If the mineral water contains much free carbonic acid, bubbles of gas are disengaged by agitating it or gently warming it.

* B. Into another portion of water a solution of *chloride of*

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[1] When the mineral water contains free carbonic acid, a strip of litmus paper being dipped in it turns red, but not so when dipped in the same water previously boiled. The litmus paper thus reddened being exposed to a gentle heat, or the reddened tincture being boiled, becomes blue again, because the carbonic acid which had turned it red volatilises. If the red colour so produced does not disappear by heating or boiling, it is a proof of the presence of a metallic salt.—ED.

[2] It should be recollected that if the mineral water contains carbonates of earths or metallic oxydes, they will be precipitated also by the lime-water, so that the precipitate may be one of carbonate of lime, or of these earths and metallic oxydes, or a mixture of all these. In order to ascertain more easily whether the precipitate produced by the lime-water re-dissolves, it is best to pour only two or three drops of lime-water, which will at first produce a precipitate, but which will instantly disappear if free carbonic acid be present.—ED.

barium and a few drops of *muriatic acid* are poured. If a precipitate of sulphate of baryta is thereby produced, the water contains a SULPHATE.

* C. A solution of nitrate of silver, to which a little nitric acid has been added, is poured into a certain quantity of the mineral water which, if it contain a COMBINATION OF CHLORINE, will become turbid or produce a white precipitate.

* When the water contains a combination of sulphur (alkaline sulphuret) a solution of nitrate of silver produces therein a precipitate of a brownish or even black colour. In order not to overlook the presence of chlorine when it exists simultaneously with a combination of sulphur, a solution of sulphate of copper is added to a portion of the water, by which means the sulphur is separated in the state of sulphuret of copper, which in the course of a little time deposits well, even though it be in trifling proportion, and it may be collected separately by filtering. It is advisable that the deposition of the sulphuret of copper should take place in a stoppered flask[1]. A little nitric acid is added to the filtered liquor, and then if it contains any combination of chlorine, the further addition of nitrate of silver produces a precipitate of chloride of silver.

* D. When the water to be analysed is well or pump water from a large town, a portion of it must be evaporated, in order to see whether it contains any NITRATES. The test is then to treat the mass obtained with a very small quantity of water, and to add thereto a solution of protosalt of iron with a great proportion of concentrated sulphuric acid (page 233).

* If during the evaporation of the mineral water a precipitate is produced, it may be removed before the liquor is completely evaporated. The precipitate contains no nitrates.

* For the purpose of ascertaining whether the mineral water contains any COMBINATION OF IODINE or of BROMINE, and considering that when this is the case, the proportions are exceed-

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[1] This precaution is recommended because recently precipitated sulphuret of copper when in contact with the air absorbs oxygen, which oxydised portion being soluble in water, of course would interfere with the subsequent operation.—ED.

ingly feeble, a considerable quantity of water must be procured. It is then evaporated almost to dryness, so as to leave only a very small quantity of mother-water, which is then treated by alcohol, and the liquor is separated from the undissolved portion, which should be once more treated by alcohol, the alcoholic solutions mixed together, and the alcohol evaporated at a very gentle heat, adding a little water from time to time in order to keep the salts in solution, and the liquor is divided into two portions, one of which is devoted to the research of *bromine*, the other to that of *iodine*, as we have said (page 424), and (page 430).

* Mineral waters seldom contain a sufficient quantity of the combinations of bromine and iodine to permit their being immediately tested for these substances. Bromine cannot be detected with certainty by the method indicated (page 424), except in the mother-waters of salt-works, and in a few saline waters of a great specific gravity.

2. DETECTION OF THE BASES.

A. To the mineral water a solution of *oxalate of potash* or of *ammonia* is added, which, if LIME be present, will produce a precipitate of oxalate of lime. If the water contains only a very small quantity of lime, a pretty long time must elapse before the precipitate can be formed.

* The liquor filtered from the oxalate of lime produced must be tested by solution of *phosphate of soda*, to which ammonia has been added in order to see whether it contains any MAGNESIA. If *muriate of ammonia* has been added to the water before testing with oxalate of potash or of ammonia, the precipitate is produced slowly, and if the proportion thus added has been large, the re-agent sometimes fails in indicating the presence of *magnesia*.

* If *lithia* is contained in the mineral water, its presence might, by the addition of solution of phosphate of soda, produce a precipitate even though magnesia be absent; but this precipitate differs from the ammonio-magnesian phosphate by the

properties which have been related (page 15). Lithia, besides, has been found hitherto in mineral waters, in such small quantities only, that in most cases, the precipitate produced by phosphate of soda is owing to magnesia. The presence of lithia, however, should subsequently be ascertained by a separate and special examination.

* B. It is important to determine even the smallest traces of iron in mineral waters, because this substance is often the real cause of the virtue of medicinal waters. When the proportion of iron is great, its presence may be detected merely by adding hydrosulphuret of ammonia, which produces a black precipitate of sulphuret of iron. It is best to mix the water with this re-agent in a flask of white glass, to cork it up, and to wait all the time necessary for the complete deposition of the sulphuret of iron. The liquid is then decanted, and the precipitate is collected on a filter, and subsequently tried before the blow-pipe, because it might in certain cases contain other substances, and even, but more rarely, other metallic sulphurets, such as SULPHURET OF MANGANESE, of ZINC, and of COPPER.

* If the quantity of iron in the mineral water is inconsiderable, hydrosulphuret of ammonia produces no black precipitate, and the liquor at most assumes a greenish colour; yet after some time, especially by leaving it in a stoppered flask and in a moderately warm place, traces of black sulphuret of iron are deposited, which may be collected on a filter, in order to examine before the blow-pipe whether it contains iron.

* Traces of protoxyde of iron too feeble to be detected by hydrosulphuret of ammonia, may be recognised by pouring a few drops of infusion of galls in the mineral waters. If, however, it contains carbonate of iron, it is necessary that it should have been recently obtained from the spring. Infusion of galls produces, not immediately, but after a little time, a purple colour. If the colouring does not augment in the space of a few hours, the quantity of iron in the water is extremely small. A deep purple or black colour bespeaks the presence of a more considerable proportion of protoxyde of iron.

* If the mineral water contains no bicarbonate of lime, the presence of iron, if in small proportion, cannot be detected, according to Philipps, by means of infusion of galls, but the addition of a little solution of carbonate of lime determines this reaction.

* The mineral waters which contain much alkaline carbonate may assume a greenish colour when treated by infusion of galls, although no iron is present.

* Iron most generally exists in mineral water in the state of carbonate of protoxyde of iron, and its presence can therefore be readily detected by means of a solution of *ferricyanide of potassium*, which produces a blue precipitate, provided always that the water, if alkaline, be saturated with an acid.

* When the mineral water has been concentrated by evaporation before precipitating it by hydrosulphuret of ammonia, infusion of galls, or by a solution of ferricyanide of potassium, the protoxyde of iron becomes converted into peroxyde of iron, and if it was combined only with carbonic acid, it is precipitated in the state of hydrated peroxyde of iron. The presence of iron may be detected in the substances which have become insoluble by the evaporation of the water. If the mineral water contain protosulphate or protochloride of iron, the quantity of hydrate of peroxyde of iron separated by evaporation is very small.

* C. *Ammonia* is added to a portion of mineral water, which re-agent precipitates CARBONATE OF LIME when contained in the water in the state of bicarbonate. This salt is contained, especially in pump or well water, in large quantities, but it may be accompanied by other substances, in very small quantity, particularly ALUMINA, STRONTIA, and LIME, combined with PHOSPHORIC ACID, and even with some FLUORIDE OF CALCIUM, &c. By leaving the water at rest for some time after the addition of ammonia, the organic matters which were contained in it are precipitated, and also the iron, in the state of peroxyde, in which case the precipitate, at first white, turns yellowish.

* MAGNESIA is not precipitated by ammonia when muriatic acid has been previously added to the water.

* Most of these substances are precipitated also without addition of ammonia, when the mineral water is boiled for a long time, and concentrated by evaporation in the open air. Often also when mineral waters are exposed to the contact of the atmospheric air, deposits are formed similar to those which are obtained by evaporating them. When these deposits can be obtained in sufficient quantity, substances may be found in them which are rare, or which exist only in very feeble proportion in the mineral water.

* When, in a qualitative analysis, the object is to detect not only the lime, but also those constituents which exist only in very small proportion in the mineral water, these deposits are treated somewhat in the same manner, as will be described in the second volume, for the quantitative analysis of mineral waters, and especially for the examination of the constituents which have become insoluble by evaporation. It rarely occurs, however, that in a simple qualitative analysis, the operator has to ascertain the presence of traces of such constituents, which are sufficiently taken into account in the analysis of quantity.

* D. A certain quantity of the mineral water is devoted to the research of fixed alkalies. If magnesia be absent, this research does not present much difficulty. If the mineral water contains a large quantity of protoxyde of iron, and if the portion of water operated upon has not been concentrated by evaporation, an aqueous solution of chlorine is poured into it, and the whole is warmed in order to convert the protoxyde of iron into peroxyde, which is not necessary when the water has been concentrated by evaporation; then, by means of a solution of carbonate of ammonia, the *lime, peroxyde of iron, phosphate of alumina,* and other constituent principles are precipitated; the liquor is then filtered, evaporated to dryness, and the residuum is ignited. The alkalies, in combination with the acids, are thus obtained. The alkali which is ordinarily met with in mineral waters is soda, yet potash and lithia are likewise found therein. The presence of

potash or of soda, whether jointly or separately contained in the mineral water, are detected by the means which have been indicated (page 659). The presence of magnesia renders this research more difficult: in such case the operator must proceed as has been said (page 660). If LITHIA exists at the same time, whether simultaneously with magnesia or not, the process is that described (page 689).

* E. A fresh quantity of mineral water is devoted to the research of AMMONIA, which is sometimes met with in these natural products. The liquid is evaporated carefully at a very gentle heat, almost to dryness, then the remaining mass is mixed with potash, for the purpose of detecting the presence of ammonia, either by the odour evolved, or by means of a glass rod moistened with muriatic acid.

* If, however, the quantity of ammonia in the mineral water is extremely feeble, the following method is the best:—A pretty considerable quantity of mineral water, which may be previously concentrated by evaporation, is treated by an excess of solution of carbonate of potash, or of soda; as soon as the effervescence (which is due to a disengagement of carbonic acid, which takes place when the water contains salts of alumina, magnesia, protoxyde of iron, &c.) has ceased, the whole is introduced in a retort, and is distilled in a receiver containing a little muriatic acid. The receiver may be changed when about half the liquid has passed over. The product of the distillation thus obtained is now evaporated to dryness at a very gentle heat, and thus after having driven off the excess of muriatic acid, muriate of ammonia is obtained, which sublimes without residuum, and in which the presence of ammonia can be detected in the ordinary way.

* Almost all mineral waters contain SILICIC ACID, which in a qualitative analysis hardly needs be separated. This acid exists generally therein in the state of animalcula.

* Sulphurous, boracic, and other acids, form an essential constituent of some mineral waters, but they are peculiar to certain countries only.

* Besides carbonic acid, sulphuretted hydrogen, and sulphurous acid, mineral waters often contain other gaseous substances in solution; they are principally NITROGEN and OXYGEN gases. But these gases are generally less abundant in the mineral waters properly so called, than in well or pump waters. They may both be disengaged by ebullition, collected, and examined.

* Independently of the constituents which have been hitherto enumerated, mineral waters very often contain ORGANIC SUBSTANCES, the presence of which causes the water to assume a yellow tinge when they are evaporated, and in consequence of which the dry salts resulting from this evaporation become blackish.

CHAPTER XIII.

QUALITATIVE ANALYSIS OF GASES.

* THE qualitative analysis of a gaseous mixture is performed either by isolating all the gases contained in the mixture or by separating simultaneously several of the gases of which it consists. This is done by means of various re-agents which produce solid or liquid bodies only when they combine with certain species of gases, whilst they have no action upon others. The same method being often employed for the quantitative analysis of gaseous mixtures, which will be treated of at length in the second volume, I shall now describe the method to be followed for the qualitative analysis of gases, more succinctly than I have done in describing the qualitative analysis of other substances.

* The experiments which it is necessary to make for the qualitative analysis of a gaseous mixture are mostly performed in glass tubes closed at one end, and which are as large but doubly as long as the test glasses used for the qualitative analysis in the humid way, and which are represented in the figure, page 580. The diameter of these tubes should not, however, be too considerable, and be such that the open extremity can be stopped with the thumb for the purpose of agitating the gas with liquid solvents.

* The gaseous mixture under examination is kept over mercury in a glass bell, small portions of the contents of which, necessary for each experiment, are transmitted into the tubes in question. In order to prevent the admixture of air with the gas whilst thus transvased, the tube is filled with mercury, and placed

upside down by the side of the bell in the mercurial trough. This trough must be capacious enough to allow of the bell to lie in it at whole length, and yet to remain covered by the mercury. The bell is then inclined gradually towards a horizontal position until the gas contained therein escapes, and the test-tube, filled with mercury, is then brought to it in such a way that the bubbles of gas escaping from the bell ascend through the mercury into the test-tube. If the necessary quantity of mercury is not at hand or to be had, the operator is obliged to use water as a substitute; the results are not the less exact on this account in most qualitative analyses. If, however, the gaseous mixture contained gases which are very soluble in water, the mercurial trough cannot be dispensed with even for a simple qualitative analysis.

* Yet there are a few gases which are absorbed or decomposed by mercury even more easily than by water; such is, for example, CHLORINE GAS. Such gases must always be collected over water.

* The gases which may be met with in qualitative analysis are the following:—OXYGEN, HYDROGEN, BICARBURET OF HYDROGEN, DICARBURET OF HYDROGEN[1], PHOSPHURETTED HYDROGEN, ARSENIURETTED HYDROGEN, ANTIMONIURETTED HYDROGEN, CARBONIC OXYDE, NITRIC OXYDE, NITROUS OXYDE, NITROGEN, MURIATIC ACID, HYDROBROMIC ACID, HYDRIODIC ACID, FLUOSILICIC ACID, BOROFLUORIC ACID, HYDROCYANIC ACID, AMMONIA, CARBONIC ACID, SULPHUROUS ACID, CHLORINE, CYANOGEN, SULPHURETTED HYDROGEN, SELENIURETTED HYDROGEN, AND TELLURETTED HYDROGEN.

* The nature of a gas can pretty easily be ascertained when not mixed with other gases. The examination of the gaseous mixture is begun by agitating it with a concentrated solution of

potash, which easily absorbs certain gases, whilst others are not absorbed by it in an appreciable manner.

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[1] Bicarburet of hydrogen and dicarburet of hydrogen are called by continental chemists *carbure dihydrique* (olefiant gas), and *carbure tetrahydrique* (light carburetted hydrogen); hydrogen being combined in the first with double the quantity of carbon contained in the second; that is to say, it consists of one volume of gaseous carbon and two volumes of hydrogen gas, condensed into one volume; its formula is accordingly CH_2. The second, on the contrary, contains one volume of gaseous carbon, and four volumes of hydrogen, condensed into half the volume of the latter, or the $\frac{2}{5}$th of the whole; its formula may then be represented by CH_4.—ED.

* To this latter series the following gases belong:—OXYGEN, HYDROGEN, BICARBURET OF HYDROGEN, DICARBURET OF HYDROGEN, PHOSPHURETTED HYDROGEN, ARSENIURETTED HYDROGEN, ANTIMONIURETTED HYDROGEN, CARBONIC OXYDE, NITRIC OXYDE, NITROUS OXYDE, AND NITROGEN.—These gases are subsequently decomposed by their more characteristic properties.

* If the gas under examination does not catch fire by the contact of a lighted body, such as a match, but causes it (the match) to burn vividly, and if a glimmering splinter being plunged into it becomes suddenly ignited, and if by mixing it with colourless nitric oxyde, ruddy fumes are formed, the gas is OXYGEN.

* If the gas under examination being set fire to burns with a bluish flame,—if it has little or no odour (the odour is always due to the presence of a foreign substance),—if when mixed with water with an equal volume of chlorine gas it is gradually absorbed under the influence of day-light by lime-water, without the latter becoming turbid or milky,—if by agitating it with solution of nitrate of silver it is not absorbed, and produces no black precipitate in it,—then the gas is HYDROGEN.

* If the gas being set fire to burns with a very brilliant flame, and if after being mixed over water with chlorine gas it is absorbed, small drops of oil being at the same time produced, imparting an ethereal smell to the water, and if an excess of lime-water added thereto does not become turbid, and lastly, if it is not absorbed by a solution of nitrate of silver, the gas is BICARBURET OF HYDROGEN (olefiant gas).

* If the gas being set fire to burns with a weak blue flame,—if by mixing it over water with chlorine gas it is decomposed in daylight (though not in the dark),—and if the lime-water added thereto becomes turbid from a production of carbonate of lime, the gas being at the same time absorbed by it [and if not absorbed by solution of nitrate of silver, nor by warming it with potassium over mercury,]—the gas is DICARBURET OF HYDROGEN (*carbure tétrahydrique*).

* PHOSPHURETTED HYDROGEN when prepared by boiling phosphorus with water and a strongly alkaline base, inflames spontaneously in the contact of the air. That which is obtained by heating aqueous phosphorous acid does not inflame spontaneously in the air; but when set fire to, it burns like the preceding with a white smoke, which reddens moistened litmus paper, a property which sufficiently distinguishes it from a great number of other gases. Its odour besides is disagreeable and quite peculiar.

* This gas being passed through a glass tube of a moderate diameter, and heated to redness on one point, is decomposed, phosphorus being deposited on the cold portion of the tube. If agitated with a solution of nitrate of silver, it is absorbed wholly and rapidly, if pure, with formation of a black precipitate, which is silver. It is likewise absorbed completely by solution of perchloride of mercury (corrosive sublimate), with formation of a yellow precipitate, which consists of perchloride of mercury, phosphuret of mercury, and water.

* Considering that phosphuretted hydrogen, which inflames spontaneously in the air, always contains some free hydrogen in more or less considerable quantity, its absorption by solution of nitrate of silver is not complete.

* ARSENIURETTED HYDROGEN burns when set fire to, and produces, when inflamed in an inverted tube, a blackish-brown deposit, the smallest particle of which is sufficient to show when heated that it is arsenic. It differs also from other gases by the property which it possesses, when agitated with solution of nitrate of silver, of being absorbed, producing at the same time a black precipitate of silver; also because it is absorbed by a solution of perchloride of mercury, producing at the same time a brownish-yellow precipitate, which consists of perchloride of mercury, of arseniuret of mercury, and of water. As, however, it always contains hydrogen, it is not completely absorbed by these two liquids. When a gas containing very little arseniuretted hydrogen is passed through a glass tube of a moderate diameter, and heated to redness on one point, it is decomposed, and deposits at a short distance from the heated point a

metallic mirror of arsenic, the smallest particles of which may be recognised by their odour as arsenic when heated.

Antimoniuretted hydrogen, when set fire to, burns with a white flame analogous to the preceding gas, and likewise when passed through a tube heated red hot at one point, deposits a mirror of metallic antimony at a short distance from the heated point. With solution of nitrate of silver it forms a black precipitate, and with that of perchloride of mercury, a white precipitate which remains for a long time in suspension. The best method of distinguishing antimoniuretted hydrogen from arseniuretted hydrogen consists in the examination of the metallic mirror produced by the decomposition of these two gases in a tube heated red hot. When that produced by arseniuretted hydrogen is dissolved in nitric acid, the acid contains then arsenious acid; if, on the contrary, that produced by antimoniuretted hydrogen is dissolved in aqua regia, this acid contains then oxyde of antimony.

* **Carbonic oxyde** being set fire to burns with a blue flame, without any appreciable smell; when mixed with a solution of nitrate of silver or over water with chlorine, it behaves in the same manner as dicarburet of hydrogen, from which it differs only because when heated with potassium over mercury it is absorbed.

* **Nitric oxyde gas** is colourless. Yet if put in contact with atmospheric air or with oxygen it produces ruddy fumes which are quite characteristic. It is absorbed by solution of sulphate of protoxyde of iron or of any other protosalt of iron, which assumes thereby a black colour. This last property is quite peculiar, and belongs to no other gas.

* **Nitrous oxyde gas** is not combustible; yet a glimmering splinter plunged into it is inflamed suddenly, as in oxygen; from which it is distinguished, because it produces no ruddy fumes when mixed with nitric oxyde gas. It is not absorbed by a solution of nitrate of silver.

* **Nitrogen gas** is not combustible, neither can it support the combustion of bodies in the state of ignition. It has on

smell, and is not acted upon by chlorine gas, nor by solution of nitrate of silver, nor in fact by any other re-agent. These negative properties are characteristic.

* The gases which are easily absorbed by a solution of potash are the following:—MURIATIC ACID, HYDROBROMIC ACID, HYDRIODIC ACID, FLUOSILICIC ACID, FLUOBORIC ACID, HYDROCYANIC ACID, AMMONIA, CARBONIC ACID, SULPHUROUS ACID, CHLORINE, CYANOGEN, SULPHURETTED HYDROGEN, SELENIURETTED HYDROGEN, and TELLURETTED HYDROGEN. These gases are more easily distinguished from each other than the other gases of which we have just been speaking. The first seven gases are soluble in very large quantity in a small proportion of water, in which they are as soluble as in a solution of potash. Considering that the other seven gases though not absolutely insoluble in water are very far from being as soluble as the others, they may thus be distinguished from each other by this property. When the first seven of these gases are mixed with other gases they may be easily recognised, after having absorbed a certain quantity of them in water, by the properties which the solution has acquired; but as we have already treated at length of such solutions in the first part of this volume, the reader is referred to it.

* The seven last gases which are not so soluble in water, are very easily distinguished from each other when mixed with other gases. *Carbonic acid, sulphurous acid,* and *chlorine* do not burn in contact with atmospheric air, whilst *cyanogen, sulphuretted, seleniuretted* and *telluretted hydrogen,* when set fire to, burn in contact with the air. The smallest traces of these four last gases may be detected by the odour which they exhale, especially cyanogen and sulphuretted hydrogen, both of which have an odour which cannot be mistaken; and besides, the other properties which have been related (pages 486, 448, 477, 479), are sufficient to distinguish these four gases with certainty from each other. As to the three gases which are not combustible, namely, *chlorine, sulphurous,* and *carbonic acids,* the two first differ from the last by their

suffocating and peculiar odour. Carbonic acid is inodorous, and agitated with lime-water it is absorbed, producing a white precipitate, which may be redissolved with effervescence by nearly all the soluble acids.

* As these various gases are easily recognised when free from foreign gases, it is not in most cases very difficult to recognise them when mixed with other gases. It is only in some cases, which will be spoken of further on, that their detection presents some difficulty; and in such circumstances a quantitative analysis must be resorted to.

* A very great number of gases having the property of mutually decomposing each other, it is not possible that all those which have been enumerated (page 739) can exist simultaneously in a gaseous mixture. Thus, chlorine destroys almost all the gases which contain hydrogen. When it is in sufficient quantity, especially under the influence of solar light, the decomposition takes place with great energy. It decomposes also some gases which contain oxygen (for example, sulphurous acid), but water must be present, for in the dry way it has no action. On the other hand, sulphurous acid decomposes sulphuretted hydrogen (page 209) and other gases of an analogous composition, but for this the presence of water is necessary also. It is hardly necessary to observe that ammoniacal gas cannot exist in presence of acid gases.

* After having collected over mercury the gaseous mixture which is intended for examination (or, if it contains chlorine, over water), it must first be agitated with a concentrated solution of potash. If nothing is absorbed, the mixture is composed of the gases which have been enumerated (page 737); if, on the contrary, the whole is absorbed, the mixture consists of the gases which have been indicated (page 739); lastly, if a portion only is absorbed, the mixture is composed of gases of both species.

ANALYSIS OF THE GAS WHICH IS NOT ABSORBED BY A SOLUTION OF POTASH.

* THE operator should first examine whether a portion of the gas which has been left after the treatment by potash can be inflamed or not in contact with the air. In the first case, it consists of combustible gases, insoluble in a solution of potash; consequently it may be HYDROGEN, CARBURET OF HYDROGEN, PHOSPHURETTED HYDROGEN, ARSENIURETTED HYDROGEN, or CARBONIC OXYDE, either singly or mixed with some of these.

* If, this effect not taking place, the gas supports the combustion of a body in a state of ignition which is plunged into it, it contains *oxygen*, or *nitrous oxyde*.

* If the mixture which is set fire to produces a more or less violent detonation, it consists of oxygen mixed with one or some of those which have hydrogen as a constituent; and if this second compound is bicarburet of hydrogen, the detonation is very violent and dangerous.

* When the gaseous mixture is neither combustible in the air nor capable of supporting the combustion of a body in a state of ignition, it is either totally or principally composed of *nitrogen*, or of *nitric oxyde*.

* A portion of the gaseous mixture which has not been absorbed by the solution of potash is agitated with a solution of nitrate of silver. If it be partially or totally absorbed by it, with formation of a black precipitate, the gas absorbed is composed either of phosphuretted hydrogen, or of arseniuretted hydrogen; it is easy, attention being paid to what we have said on the subject (page 738), to recognise which of these two gases is contained in the mixture. In such a case the portion which has not been absorbed by the solution of nitrate of silver consists of hydrogen gas only, with which these gases are almost generally mixed.

* If the mixture is inflammable in the contact of atmospheric air, and yet is not absorbed by solution of nitrate of silver, chlorine is added to it over water. When the mixture contains bicarburet of hydrogen, it is easily recognised as such by the

drops of oil which are formed, and the ethereal odour which the water impregnated with the gas, acquires. If the gas, mixed with chlorine, after remaining exposed to daylight, is absorbed by an excess of lime-water, which at the same time becomes turbid, it may contain either dicarburet of hydrogen or carbonic oxyde. It is difficult in qualitative analysis to determine which of these two gases is contained in the mixture, or whether both of them are contained therein. The only means of effecting it consists in introducing a small piece of potassium in the dry mixture of gases, and in heating it over mercury. The oxyde of carbon is thus absorbed, whilst the carburet of hydrogen remains unaltered (page 737). When, independently of this gas, hydrogen exists in the mixture in the free state, its presence cannot be ascertained in qualitative analysis.

* If the gas, which is combustible in the air after being mixed over water with chlorine gas, is absorbed after a more or less considerable time, but without producing a white precipitate in the lime-water which has been added in excess, the gas is hydrogen.

* When the mixture is incombustible in contact with the air, but detonates when set fire to, nitric oxyde is to be mixed with it. If ruddy fumes are thus produced, and absorption takes place, it is a sign that oxygen is present. That of nitric oxyde is also easily recognised by introducing oxygen gas or atmospheric air with the mixture. Yet nitric oxyde may also be recognised, because it is absorbed by a solution of protosalt of iron, and the black colour which it communicates to the latter.

* If anything remains after the gaseous mixture has been successively treated by a solution of nitrate of silver, by gaseous chlorine, then by oxygen or nitric oxyde, it can only be nitrous oxyde, or nitrogen. In the first case, the gas supports combustion; in the second, it does not. If, however, the two gases exist simultaneously in the mixture, they may be separated from each other, and recognised, by adding to the mixture about one-fourth of its volume of alcohol, and agitating the whole for a long time; the nitrous oxyde gas alone is absorbed, and the nitrogen remains.

ANALYSIS OF THE GAS ABSORBED BY THE SOLUTION OF POTASH.

* The qualitative analysis of the solution of the gases which have been enumerated (page 739), might *"à la rigueur"* be performed in the manner described in Chapters VIII. and XI. of this Second Part; for, with the exception of ammonia, the solutions of these gases in water produce with potash combinations the acid elements of which may be detected, according to the methods which have been described in those two chapters. There are some cases, however, in which certain gases can be more easily recognised in the gaseous mixture itself, by treating it with various re-agents.

* Most of the gases which the solution of potash absorbs are of an acid nature. The gases which are strongly acid are absorbed in the dry state over mercury by borax, though in most cases very slowly (for example, muriatic acid, sulphurous acid, &c.) The gases which are feebly acid, such as carbonic acid and sulphuretted hydrogen, are not absorbed by borax. This is therefore a good means, in certain cases, of distinguishing them from each other.

* If, before putting the gaseous mixture in contact with the solution of potash, it be treated by a very small quantity of water, the latter dissolves certain gases largely, whilst others, enumerated (page 739), are dissolved by it only in much less considerable quantity.

* Therefore, after having treated the gaseous mixture with very little water, a portion of the gas which has not been absorbed is agitated with lime-water, by which it is absorbed in toto. If the lime-water becomes turbid or milky, it is a proof of the presence of CARBONIC ACID, by which property it is generally detected when mixed with other gases, even with such as are not absorbed by a solution of potash.

* A portion of the gas is agitated with a solution of *acetate of lead.* If a black precipitate takes place, and if the gas is absorbed either wholly or partially, the conclusion is, that it

contains SULPHURETTED HYDROGEN, the least quantity of which is detected besides by its odour, and if in large proportion, by the properties which it possesses of burning in the contact of the air with a blue flame, and with an odour of sulphurous acid. SELENIURETTED and TELLURETTED HYDROGEN behave in the same manner, but they have not the latter property.

* When the gas destroys the blue colour of tincture of litmus, or imparts a yellow colour to the liquor, and also when it is wholly or partially absorbable by mercury, CHLORINE GAS is present.

* If the gas has the well-known odour of burning sulphur; if it is absorbed by red lead, or by the brown oxyde of lead ($Pb\ O_2$), as well as by borax, it is SULPHUROUS ACID GAS.

* In order to ascertain whether the mixture contains any CYANOGEN GAS, it is passed through solution of potash, which will absorb it, and to this solution one of sulphate of protoxyde of iron, containing a small quantity of peroxyde, is added. A little dilute sulphuric or muriatic acid is next poured in, so as to render the liquid acid. If a blue precipitate is produced, the mixture contains cyanogen gas. It is advisable, before making these experiments, to introduce some red oxyde of mercury into the gas, for the purpose of absorbing the vapours of hydrocyanic acid which might exist, because otherwise the presence of that substance might subsequently give rise to phenomena analogous to those which cyanogen gas produces. Cyanogen gas is not absorbed by peroxyde of mercury.

* The gases largely soluble in a small quantity of water, and which have been enumerated (page 739), are easily recognised, even when mixed with several others.

* When at the time of its absorption by water the gas deposits gelatinous flakes, which are easily identified as silicic acid, the conclusion is, that it contains FLUOSILICIC GAS.

* If the solution of the gas in a small quantity of water is mixed with alcohol, and if the latter being set fire to burns with a green flame, it is a proof of the presence of FLUOBORIC GAS.

* If the solution of the gas in a small quantity of water, or better still, its solution in one of potash, being mixed with nitric

acid and a solution of starch, produces a blue colour with the latter, it is a sign of the presence of HYDRIODIC ACID GAS, which, however, is decomposed by mercury, and which cannot be collected over water on account of its great solubility in this menstruum.

* If chlorine gas, or an aqueous solution of chlorine, being added to the gas, imparts a brown colour to the solution, which colour disappears by agitating the solution with ether, which takes it up, it is a certain indication of the presence of HYDROBROMIC ACID GAS.

* If the solution of the gas in water is precipitated white by a solution of nitrate of silver, and if the precipitate so produced is insoluble in dilute nitric acid, but soluble in ammonia, and if the absence of hydrobromic and hydrocyanic acid gases have been previously ascertained, the gas contains MURIATIC ACID, the existence of which, however, is difficultly ascertained in presence of hydrobromic acid. In such a case, the operator should proceed with the aqueous solution of the gas, previously saturated with potash and evaporated, as we have said (page 424.)

* If the solution of the gas in one of potash behaves like that of cyanogen in this re-agent, but yet if the gas is absorbed, either wholly or partially, by peroxyde of mercury, the operator may rest assured that it contained HYDROCYANIC ACID.

* Lastly, if white fumes are produced in the gas when either concentrated muriatic acid or muriatic acid gas are introduced into it, and if this phenomenon is accompanied by a condensation, the gas contains ammonia, which gas, however, cannot exist in presence of an acid gas, and a small quantity of which may already be detected by its peculiar odour.

ERRATUM.

Note 1st, page 48, instead of "as with *potash*," read "as with *alumina*."

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